

MSc Thesis

RATIONAL DESIGN OF SILVER/PLATINUM
CORE/SHELL NANOPARTICLES AS CATALYSTS FOR
ELECTROCHEMICAL HYDROGEN PRODUCTION AND
OXYGEN REDUCTION REACTION

by

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ABSTRACT

RATIONAL DESIGN OF SILVER/PLATINUM CORE/SHELL NANOPARTICLES AS CATALYSTS FOR ELECTROCHEMICAL HYDROGEN PRODUCTION AND OXYGEN REDUCTION REACTION

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Pt based electrodes are used in the hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) owing to their stability and high efficiency with low overpotential. However, the amount of Pt used in the electrocatalysts should be reduced by preserving their catalytic efficiency so that Pt based electrodes find more widespread use in commercial applications. To achieve this goal, the reduction of particle size of Pt electrocatalysts is a promising way, but there are still a high percent catalytically intact Pt atoms remained in the core of small Pt NPs. In this respect, instead of using monometallic Pt NPs, the rational design of Pt core-shell NPs is highly promising because a cheaper metal is used in the core and less amount of Pt with higher efficiency is used as a shell and thus overall activity can be enhanced due to structural changes. For this purpose, in this study, we synthesized Ag/Pt core/shell NPs by using surfactant-assisted solvothermal method and then assembled the yielded Ag/Pt core/shell NPs on commercially available high surface area carbon support. The performance of as-prepared C-Ag/Pt and Pt hollow catalysts that is obtained by the

acid-treatment of C-Ag/Pt were tested in HER and ORR. In order to modify Pt from core/shell structure, two methods, chemical etching and electrochemical leaching, were applied to remove Ag from the core. Pt hollow structures were obtained via chemical leaching whereas electrochemical leaching gave featureless NPs. Electrochemical activity tests revealed that both electrochemical and chemical leaching gives higher activity in HER in acidic electrolyte. More specifically, the cathodic activity for HER shows that the overpotential required to obtain -10 mA/cm^2 is reduced by 35 mV for electrochemically leached Pt NPs while it is 85 mV for chemically leached Pt NPs. In both HER and ORR, the structural changes in the surface region are more effective to tune the activity rather than the Pt amount. Improved activity is associated with the modified electronic properties of the Pt skin layer which can also be adjusted by proper selection of particle size.

Keywords: Hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), modified C-Ag/Pt core/shell NPs, electrochemical activity, rotating disc electrode (RDE)

ÖZETÇE

ELEKTROKİMYASAL HİDROJEN ÜRETİMİ ve OKSİJEN İNDİRGEME TEPKİMELERİ İÇİN KATALİZÖR OLARAK GÜMÜŞ/PLATİN ÇEKİRDEK/KABUK NANOPARÇACIKLARININ AKILCI TASARIMI

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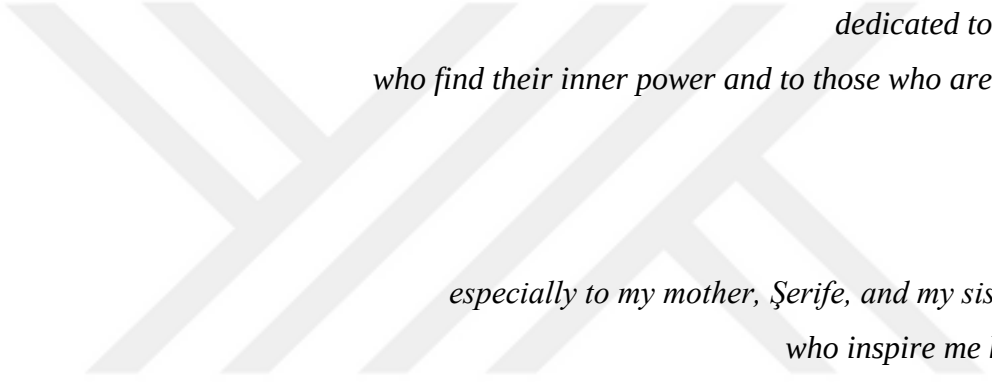
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Platin (Pt) bazlı elektrotlar sahip oldukları kararlı yapıları ve düşük aşırı gerilimleri sayesinde gösterdikleri yüksek performansları nedeniyle hidrojen üretim reaksiyonunda (HER) ve oksijen indirgeme reaksiyonunda (ORR) kullanılmaktadır. Bununla birlikte, Pt bazlı elektrotların ticari uygulamalarda daha yaygın kullanım alanı bulması için elektrokatalizörlerde kullanılan Pt miktarının, katalitik performanslarının korunarak azaltılması gerekmektedir. Bu amaca ulaşmak için, Pt elektrokatalizörlerinin parçacık boyutunun küçültülmesi umut vadeden bir yoldur; ancak yine de küçük Pt nanoparçacıklarının (NP) çekirdeğinde kalan, katalitik olarak inaktif Pt atomlarının yüzdesi halen yüksektir. Bu bağlamda, monometalik Pt NP'lerin kullanılması yerine çekirdekte daha ucuz bir metalin yer aldığı çekirdek-kabuk yapısında bimetalik Pt NP'lerinin akılcı bir tasarım ile sentezlenmesi, oldukça ümit vericidir. Böylece daha az miktarda Pt'nin, çok ince kabuk olarak daha yüksek verimle kullanılması sağlanabilir. Böylece Pt elektrokatalizörün aktifliği yapısal değişiklikler ile geliştirilebilir. Bu amaçla, bu tez çalışmasında, bir yüzey-aktif madde içerikli

solvotermal yöntem kullanarak gümüş/platin (Ag/Pt) çekirdek/kabuk NP'leri sentezlendi. Daha sonra, elde edilen Ag/Pt çekirdek/kabuk NP'leri ticari olarak temin edilebilen geniş yüzey alanına sahip karbon destek üzerine tutturuldu. C-Ag/Pt ve C-Ag/Pt'nin asit ile muamele edilmesi yolu ile elde edilen Pt oyuklu katalizörlerin performansı, HER ve ORR'de test edildi. Ag/Pt çekirdek/kabuk nanopartikül yapısında yer alan gümüşü çekirdekten uzaklaştırmak yolu ile Pt'yi modifiye etmek için kimyasal aşındırma ve elektrokimyasal ayırma metotları kullanılmıştır. Kimyasal ayırma ile oyuklu-Pt yapısı elde edilirken, elektrokimyasal ayırma ile özelliksiz NP'ler elde edilmiştir. Elektrokimyasal performans testleri, HER'de hem elektrokimyasal hem de kimyasal ayırma için asidik elektrolitte daha yüksek aktiflik gösterdiğini ortaya koydu. Daha spesifik olarak, HER katodik aktifliği 10 mA/cm^2 elde etmek için gereken aşırı gerilimin elektrokimyasal olarak süzölmüş Pt NP'lerde 35 mV azaldığını; diğer yandan azalmanın kimyasal olarak süzölmüş Pt NP'lerde de 85 mV olduğunu göstermiştir. Hem HER hem de ORR'de yüzey bölgesindeki yapısal değişiklikler aktiviteyi değiştirmek için Pt miktarına kıyasla daha etkili olduğu ortaya koyulmuştur. Geliştirilmiş aktiflik, Pt yüzey katmanının modifiye edilmiş elektriksel özellikleri ile ilgilidir ve bu katman da parçacık boyutunun doğru seçilmesi ile düzenlenebilir.

Anahtar sözcükler: Hidrojen üretim reaksiyonu, oksijen indirgeme reaksiyonu, modifiye edilmiş C-Ag/Pt çekirdek/kabuk nanoparçacıkları, elektrokimyasal aktivite, döner disk elektrotu



*dedicated to all women
who find their inner power and to those who are still trying*

*especially to my mother, Şerife, and my sister, Canan
who inspire me how to find*



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Human is a social being. In the social life, only basic and daily knowledge exists. This common sense knowledge is based on prejudices by definition. Scientific work, on the other hand, tries to go beyond this daily and false conscience by establishing an alternative consciousness based on causal relationship between phenomenon and event. All this process requires to complex thinking. It is important to realize that all complex ideas in science depend on basic principles, law and assumptions. But, reaching over this simplicity needs an infinite ability. This principle is called “Ockham’s Razor”.

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CHAPTER 1

INTRODUCTION

1.1 Fuel Cells

The increase in worldwide energy demand becomes one of the major challenges of the twenty first century due to population growth and rises in living standards [1]. The main source of energy is supplied via fossil fuels in today's world. Although fossil fuels are advantageous since obtaining required energy from them is quite straightforward due to simple combustion process, they are inadequate to satisfy the demand due to their limiting resources and economic issues such as increasing price as a result of changing political situations in the world. Moreover, in the environmental point of view, fossil fuels destroy the world by causing the global warming via greenhouse gases emission. All those critical reasons lead us to a need in alternative energy with clean energy resources.

Fuel cell offers clean alternative energy with zero emission. It is a device that converts the chemical energy of the fuel to the electrical energy. It is a galvanic cell where reactions occur spontaneously without needing any power input. Therefore, it promises electricity with no dependency of stable station. Proton exchange membrane fuel cell (PEMFC), a type of a fuel cell, is easy to operate and gives high power density. PEMFC uses hydrogen and oxygen as fuels to generate electricity. Hence, hydrogen and oxygen are inputs while water, heat and electricity are outputs of the overall reaction which is basically the combustion of hydrogen.

In briefly, the working principle of PEMFC is quite straightforward. Hydrogen gas enters the system from anodic side. It ionizes and forms proton, H^+ , and electron as a result of hydrogen oxidation reaction. The electrons pass through the anodic side

where oxygen gas, generally air is used as a source of oxygen, exists with the help of external circuit whereas protons, H^+ , uses the polymer membrane between the electrodes as a road to reach the anode. Oxygen gas takes the electrons and H^+ and forms water which is the only by-product of PEMFC. The motion of the electrons via external circuit is the electricity generated while water is the product of the total reaction. Each PEMFC generates less than 1V. Thus, there are more cells needed to generate more energy by series connection in application point of view.

Fuel cell has mainly transportation applications such as electrical vehicles, hydrogen cars and so on. Therefore, even though fuel cell promises silent operation and higher efficiency compared to internal combustion engine, one of the main challenging issue about PEMFC is the durability which can be defined as the performance of fuel cell over time. It decreases as time passes and the effect is irreversible since the reason is aging [2]. The other challenge is the cost of the system; however, when taking into consideration about the long-term electricity cost, this item will be no longer an issue.

Consequently, in order to operate PEMFC, hydrogen and oxygen are needed. Since atmosphere has oxygen, air can be used as oxygen source for cathodic side. However, hydrogen should be obtained by extracting from which it exists. Hence, using pollutant free method to produce hydrogen makes sense while searching for alternative resources against global warming.

“Yes, my friends. I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable. (...) Water will be the coal of the future.”

As the character named Cyrus Smith in the novel named Mysterious Island written by Jules Verne in 1874 indicated, water splitting has precious role in hydrogen economy and fuel cell as an alternative energy resource in today's world. Hydrogen economy is promising due to high gravimetric density and less harmful to the environment [3]. Therefore, water splitting for electrochemical hydrogen production, known as

hydrogen evolution reaction (HER), has been considered as a nonpolluting and efficient method. On the other hand, oxygen reduction reaction (ORR) is the main reaction of PEMFC occurring in cathodic side. It is a challenging reaction since it has lots of side reactions with slow reaction rate. Therefore, main obstacle for efficiency of fuel cell is the low rate of oxygen reduction reaction. Pt based electrodes used in commercial applications have excellent performance for both hydrogen evolution and oxygen reduction reaction. Consequently, the common aim among scientists is to increase the efficiency of electrochemical hydrogen production and oxygen reduction reaction by finding alternative catalysts for widespread commercial usage. Similarly, this project also aims to enhance the electrochemical activity of HER and ORR by using engineered Pt nanoparticles.

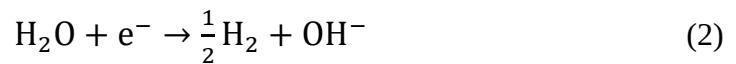
1.2 Hydrogen Evolution Reaction

In water splitting, oxygen formation occurs in anodic side while hydrogen forms in cathodic side. The electrochemical hydrogen production from water is HER.

In acidic solutions where pH is less than 7, hydrogen forms as a result of proton, H^+ , presence.



On the other hand, water is the source of formed hydrogen when pH is more than 7 [4].



There are three rate determining reaction steps for HER in both acid and alkaline solutions: Volmer, Heyrovsky and Tafel reactions. Volmer step occurs when proton adsorbs on the electrode. It is the first step of the hydrogen evolution reaction regardless of the pH of the solution. After this step, reaction proceeds either Tafel or Heyrovsky steps. In Tafel reaction, another proton comes to electrode surface and

adsorbs there. Hydrogen forms with those adsorbed protons on the electrode surface. On the other hand, Heyrovsky step is where another proton adsorbs by the first adsorbed proton rather than electrode surface and thereby, molecular hydrogen forms directly. In any case, the key point that determines the reaction kinetics and thermodynamics is the strength of metal-adsorbed hydrogen bond since it forms and breaks in both reaction pathway[5]. On the other hand, Volmer-Tafel reaction mechanism is more efficient than Volmer-Heyrovsky mechanism. For instance, the onset potential of the Tafel step is around 30 mV while it is about 140 mV for Heyrovsky step.

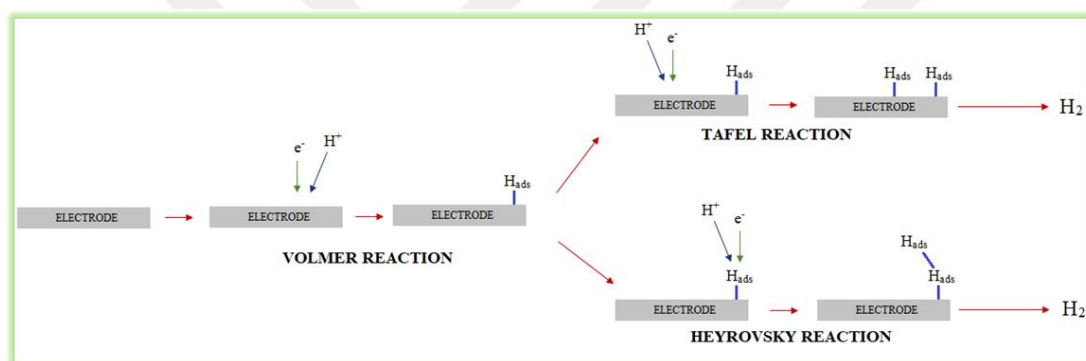


Figure 1.1 Schematic of HER Mechanism

Related reaction steps are also shown in Table 1.

Table 1.1 Reactions of the mechanism in hydrogen evolution reaction

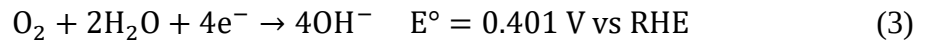
	In acidic solutions	In alkaline solutions
Volmer Reaction	$H_{aq}^+ + e^- \leftrightarrow H_{ads}$	$H_2O + e^- \leftrightarrow H_{ads} + OH^-$
Heyrovsky Reaction	$H_{ads} + H_{aq}^+ + e^- \leftrightarrow H_{2(g)}$	$H_{ads} + H_2O + e^- \leftrightarrow H_{2(g)} + OH^-$
Tafel Reaction	$H_{ads} + H_{ads} \leftrightarrow H_{2(g)}$	$H_{ads} + H_{ads} \leftrightarrow H_{2(g)}$
Overall Reaction	$2H^+ + 2e^- \rightarrow H_2$	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

1.3 Oxygen Reduction Reaction

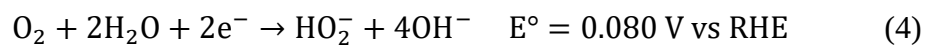
The electrochemical reduction reaction occurring in the cathodic side of PEMFC is ORR. It has a slow rate which affects the performance of fuel cells. The reaction has mainly two different paths to follow in aqueous solutions: direct pathway via four-electron process or indirect reaction from oxygen to peroxide via two-electron transfer. The efficient path is the direct water production with four-electron transfer.

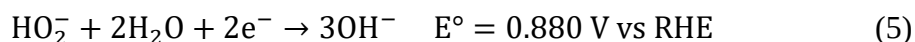
The steps of ORR in alkaline media are shown in the following [6].

The direct pathway with four-electron transfer,



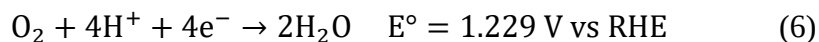
The indirect pathway with two-electron transfer,





The steps of ORR in acidic media are shown in the following [6].

The direct pathway with four-electron transfer,



The indirect pathway with two-electron transfer,



1.4 Nanocatalysts for Electrochemical Applications

Nanocatalysts have a tremendous attraction due to their ease in synthesis and modifications with various methods in catalyst area [7]. According to prediction of physicists based on quantum-mechanical rules, nanoparticles (NPs), particularly in the diameter range of 1-10 nm, exhibit their electronic band structure which depends on particle size, interparticle distance and shape of the nanoparticle [8]. Such control parameters have significant importance since the potential developments can lead increase in diversity of applications for green economy.

In general, nanocatalysts can be classified based on their dimensions which are 0D, 1D, 2D and 3D such as grains, quantum dots, NPs as 0D, nanotubes, nanowires, nanorods as 1D, nanosheets, nanowalls as 2D and nanoballs, nanoflowers as 3D [9]. Nanoparticles are quite attractive as electrocatalysts since they have high surface to volume ratio which is an extremely important parameter since the electrochemical reactions occur in the surface of the catalyst material.

Monometallic NPs consist of single metals. The type of metal determines the properties of the nanoparticles most in an addition to particle size and the shape [10]. On the other hand, bimetallic nanoparticles are the ones consisting of two metals. They can be categorized as alloys and core-shell structures.

Alloys are the combination of at least two metallic elements to enhance the certain properties of monometallic materials. The atomic size difference is a major factor affecting the formation and structure of alloy. Alloys can be categorized based on the difference in particle diameter of constituents which are substitutional alloying and interstitial alloying. For instance, alloying Pt with Ag is substitutional alloying since the atomic radius of Pt is less than Ag whereas alloying Pt with Co is an example of interstitial alloying since the atomic radius of Pt is more than Co [11].

NPs containing inner material in the core and outer material as a shell are called as core-shell NPs. The interaction between core and shell material results in different properties of the material. Core-shell NPs present a great diversity about the material properties not only with the modifications in surface structure of shell to reach more efficient catalytic performance but also with the synergy between core and shell material which also effects the yield and selectivity of the catalysts [12]. Thus, core-shell NPs are promising due to their possible superior performance. For instance, S. Sun et al. synthesized Pd/FePt NPs which has Pd as a core and FePt alloy as a for ORR. They obtained the controlled nucleation growth of FePt alloy structure on Pd with the help of Fe precursor, $\text{Fe}(\text{CO})_5$ since otherwise they cannot control separately formed and precipitated Pt NPs. They also arranged precursor amount such a way that there is no multiple nucleation growth such as separate Pt nanoparticle formation in an addition to Pd/FePt core-shell structure. Moreover, they used acetic acid treatment for the removal of surfactant; however, the acid leached a huge amount of Fe as well which doesn't affect the activity result since their claim is that the reason of enhanced ORR activity is not due to the alloy in the shell but Pd in the core. They played with the shell thickness and obtained better onset potential for ORR by using RDE compared to commercial Pt-C with 1 nm and 2 nm as shell thicknesses while 3 nm as shell thickness gives slightly worse catalytic activity. They show the structure of synthesized NPs by using HAADF-STEM images [13].

The properties of the NPs such as electronical, optical and mechanical can vary by differing the constituents [14]. Therefore, bimetallic NPs have an essential role for

better catalytic performance by improving the properties of single-metal catalysts. The improvements on electronic structure can be explained via three fundamental effects: ensemble, ligand and geometric [15]. Ensemble effects are related to the presence of dissimilar atoms existing individually or in a group within a certain geometry contributing the surface adsorption of the catalyst whereas ligand effects are related to the atomic vicinity that affects the charge transfer by changing the electronic structure. On the other hand, geometric effect is related to the structural difference in surface atoms which results in the difference in activity due to distinct arrangements (i.e. strain effect) [15]. If the catalyst particle is small enough (i.e. less than 5 nm), the lattice strain effects can no longer be neglected since it affects the surface structure of the metallic NPs. The change in surface structure due to lattice strain is promising to tune the NPs in order to enhance the reactivity of the surface reactions since it also affects the energy of the bonding and thus the chemisorption energy between the surface and the adsorbent. The lattice mismatch, occurring when there is a difference in lattice constants in heterostructures, contributes the most to the strain in bimetallic NPs, particularly for core-shell structures due to the difference in lattice constants between the core and shell. Compressive and tensile strains are two types of strain effect regarding to the difference in the structure and particle sizes of constituents of alloys or core-shell structures. Compressive strain occurs when small substitutional atoms place to the structure while tensile strain presents due to large atoms added [16].

H. You et. al. studied strain effect in AgPt alloy NPs by showing the effect of lattice distortion via XRD and TEM. They observed twin planes in their AgPt alloy, whose average particle size is 2 nm based on HRTEM, as a result of Ag integration to Pt lattice which is common structure in noble metals to reduce the total energy, particularly in bimetallic alloys containing Pt after high temperature treatment. They observed that twin planes due to lattice distortion causes peak shift in XRD to higher angles [17].

There is a reverse proportionality between the surface energy and the particle size of metal. For instance, the d-band center of transition metals shifts either upward or

downward due to the strain effect. This shift results in the change of surface energy and affects adsorption [16].

1.5 Bimetallic Nanoparticles Involving Pt in Electrochemical Applications

Bimetallic NPs offer a promising future for electrocatalysts, particularly for ORR and HER.

S. Guo et al. suggested that MPt alloys, where M is Fe, Co or Ni, improve catalytic activity for ORR compared to Pt or any other MPt alloys since M brings about the shift in d-band center of Pt which lowers the adsorption degree of oxygenated species such as OH and leads to higher active sites for oxygen adsorption [18].

V. Stamenkovic et al. studied with the polycrystalline alloy films of Pt₃M where M refers to Ni, Co, Fe and Ti to improve electrochemical activity of ORR. They annealed the alloys under UHV at 1000K which enabled the detailed characterization. Therefore, they showed that Pt rich regions changed from layer to layer due to segregation which results in the descending concentration profile of Pt from first layer to bulk. They proved that alloying Pt with 3d metals improve ORR activity due to modifications in electronic structure of surface Pt atoms. Moreover, they developed a kinetic model on the basis of DFT calculations [19].

Elisa Navarro-Flores and coworkers showed the increase in electrochemical activity compared to pure Ni when they used NiM alloy where M represents left-hand side transition metals such as Fe, Mo or W in hydrogen evolution reaction. For this purpose, they modified the electronic structure of nickel by alloying with tungsten by changing its electron density in d-orbitals which leads to higher surface roughness and thereby, higher electrocatalytic yield. Also, incorporation the transition metals with Ni's FCC structure result in the increase of crystallinity which improves HER as well [5].

D. Wang and her colleagues suggested the enhanced nanocatalytic performance for ORR by synthesizing C-Pt core-shell NPs whose shell 2-3 nm thick Pt while whose intermetallic core consists of Pt₃Co alloy by proving the highest mass and specific activity among C-Pt systems. They used impregnation reduction method with varying temperature and mixture of hydrogen and nitrogen atmosphere after heat treatment at 400°C and 700°C, separately, for controlled synthesis of Pt₃Co-C NPs. They show the formed alloy structure, the existence of Co on face-centered cubic Pt, and the 0.8% of compressive lattice strain effect compared to C-Pt from XRD results by indicating the peak shifts and calculating the lattice parameter [20].

B. Zhang et. al synthesized Pt₃Co/Pt core/shell NPs via controlled thermal treatment method to see the importance of surface composition of Pt by creating 2 or 3 atomic layer of Pt-shell as a result of the surface segregation in electrochemical reactions such as ORR [21].

1.6 Colloidal Synthesis of Bimetallic Nanoparticles Containing Pt

Metallic NPs are synthesized via physical or chemical synthesis. The division of bulk material into the nanoparticles is the main procedure behind the physical methods while nanoparticles are obtained via the reduction of metal ions to metal atoms in chemical synthesis. The chemical method is used more widespread since it is easier to control the aggregation process and therefore, easier to obtain monodispersed NPs. With this controlled manner in chemical method, the control of particle size and the distribution is quite important since it mainly affects the activity and selectivity of catalysts [22]. In other words, the preparation methods determine the structure of NPs such as size and shape which is important specially for bimetallic NPs since controlling the parameters increase the possibility of diversity in physical properties [23]. Colloidal synthesis enables the controlled growth and provides monodisperse NPs.

A colloid is a system consisting of one substance finely divided and distributed evenly throughout a second substance. Stability is the key word in the colloid systems. From

thermodynamic aspect, while solutions are thermodynamically stable with negative Gibb's energy and dispersions are unstable with positive Gibb's energy, colloids are kinetically stable dispersions since the mixing process occurs slow enough. There are important concepts that help the understanding of colloid systems. The first one is floc which is the aggregate of individual colloidal particles whose structure is relatively loose and open. The process is reversible meaning that it has some amount of energy input to return its original state. The process of floc formation is called as flocculation. The second one is coagulum which is the aggregate particles whose structure is relatively tight and dense due to losing the maintenance of the dispersed phase. The process is irreversible and therefore, there is no return to its original state regardless of the amount of energy input. The process of coagulum formation is called as coagulation. In addition to those concepts, parameters affecting stability of colloids are temperature, particle size, concentration and dispersion medium.

The stability is reached with a balance between forces such as buoyancy, gravitational, steric and electrostatic in colloidal systems. Therefore, the first important element is the reducing agent which enables metal ions to turn into metal atoms via proper chemical reduction reaction. The second important element is the stabilizers such as ligands or polymers in order to be able to control the reduction rate and the aggregation by steric effects.

1.7 Why Pt?

In HER, the crucial step is H adsorption on the catalyst surface which determines the importance of catalyst type. The adsorption free energy of H on Pt at standard conditions (at 1 bar, 300K and pH=0) at equilibrium is approximately 0 [24]. Hence, Pt shows the best performance for HER with its high current density at low overpotentials. More specifically, the exchange current density of HER in H₂SO₄ for Pt as an electrocatalyst is between 5×10^{-4} to 10^{-3} Acm⁻². Also, at low overpotentials, the Tafel slope is 30 mVdec⁻¹ while it is 120 mVdec⁻¹ at high overpotentials. Moreover,

the exchange current density is observed as $10^{-3} \text{ A cm}^{-2}$ for only one Tafel slope of 29 mV dec^{-1} . The given values shows that the reaction follows Volmer-Tafel at low overpotentials while the mechanism is Volmer-Heyrovsky at high overpotentials. [4]

However, it has several disadvantages that push scientist to find new material or to modify in order to eliminate the negative sides of Pt. The major challenge is the fact that Pt is cost-ineffective. It has also problem with its scarcity.

Despite of these negative sides, Pt is the most common one after optimization of cost, durability and efficiency as a fuel cell catalyst. It is claimed that the real cost of fuel cell doesn't originate from the catalysts cost but it is due to the operating voltage cost. For instance, to improve operating voltage as 0.1 V can save ten times more in electricity costs due to decrease in consumption compared to catalysts expenses. Therefore, the main issue here is not just to reduce the noble metal cost but also increase the efficiency of the reaction to decrease the operating cost. Hence, Pt is still the most proper choice as HER catalyst [24].

1.8 Modifying Pt from core/shell nanoparticles for electrochemical applications

The idea of finding optimum catalyst for HER and ORR is the one of the most significant issue for electrochemical applications. Bimetallic NPs provide wide range of alternatives to realize the concept. At this point, bimetallic NPs itself such as alloys and core-shell NPs are indeed promising. However, taking bimetallic NPs, either alloys or core-shells, one step further such as removing the less reactive component causes structural changes such as higher surface to volume ratio and better electrical properties of remained constituent which can improve the electrochemical activity even better. For instance, the hollow structure as a certain shaped particle is encouraging in modified NPs view since it has greater surface area with low loading density. Since Pt is the most favorite catalyst, modifying Pt from bimetallic core/shell NPs to change the surface reactivity is quite convenient.

Based on the idea above, S. Koh and P. Strasser presented dealloyed Pt from C-Pt alloy NPs by applying electrochemical method and even though they observed Pt-oxides formation after the dealloying process, they also saw that no Cu remained in the surface afterwards based on cyclic voltammetry measurements. Therefore, they demonstrated the significant shift towards less overpotential in electrochemical activity tests of ORR in RDE for dealloyed Pt catalysts compared to pure Pt electrodes [25].

Aim of the Study

This study aims to synthesize Ag/Pt core/shell NPs and well-shaped hollow Pt NPs by using Ag seeds and investigate their electrochemical activity towards HER and ORR. The study offers the new synthesis recipe, which is a surfactant-assisted solvothermal seeded growth with oleyl amine, for Ag/Pt core/shell NPs to the literature. Also, it is a detailed study containing the synthesis of Ag/Pt core/shell NPs, modified Pt NPs from these core/shell NPs via two different methods, i.e. electrochemical and chemical leaching and their activity tests for ORR as a fuel cell cathode and HER as a water splitting cathode in electrochemical applications. Moreover, hollow Pt NPs obtained from Ag/Pt core/shell NPs for HER is a new contribution to the literature. Meanwhile, the study points out the effect of segregation and leftover Ag in skin layer observed as a result of two different modification methods.

The outline of the thesis is as follows:

Chapter 2 – Methodology is given to have a basic idea about the instruments used for characterization and electrochemical activity tests by explaining the basic theory behind them. For this purpose, first, a brief electrochemistry review and the methods for electrochemical activity test such as linear sweep voltammetry, cyclic voltammetry and rotating disc electrode were introduced. Then, the theoretical background of characterization instruments was summarized.

Chapter 3 - Synthesis and Characterization of Carbon Supported Ag/Pt Core/Shell Nanoparticles is written to explain the synthesis methods and obtained results. Therefore, characterization techniques to understand the structure and the components of catalysts and the activity tests for HER and ORR to examine whether the catalysts is proper for the predictions were main aspects of this chapter.

Chapter 4 - Synthesis and Characterization of Modified Pt Nanoparticles in Electrochemical Applications is written to understand the modifications applied to C-PtC-Ag/Pt core/shell NPs starting from the synthesis. The changes in the structure of modified catalyst compared to core/shell NPs were discussed by taking characterization technique into an account. Activity tests were used to understand the functions of catalysts in HER and ORR.

Chapter 5 – Conclusion contains the summary of the study and focuses on the future works that will be done within the context of this project.

CHAPTER 2

METHODOLOGY

2.1 Kinetics of Electrochemical Processes

Electrochemistry focuses on the charge transfer processes at the interface. Electrochemical reactions occur at the interface between the electronic conductor, which is called as electrode, and the ionic conductor, which is electrolyte. Electrochemical cell is the system where the nonspontaneous electrochemical reactions, in which Gibb's free energy is more than zero, driven by applying external potential occur. There are several factors affecting the reaction rate which mainly are the mass transfer between the bulk and the electrode surface, electrode transfer at the electrode surface and surface reactions such as adsorption, desorption or electrodeposition.

The electrochemical cell can basically be conducted via three electrode system consisting of working electrode where the reaction is controlled, counter or auxiliary electrode and the reference electrode which has known potential for a reference state. Some examples of reference electrodes mainly used are reversible hydrogen electrode (RHE), saturated calomel electrode (SCE), mercury-mercurous sulfate electrode and silver-silver chloride electrode. There are conversion equations from one reference electrode to another one. For instance, the conversion from Ag/AgCl electrode to reversible hydrogen electrode is in the equation (9). [26]

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E_{\text{Ag/AgCl}}^{\circ} \quad (9)$$

In order to categorize reactions, standard electrode potentials are determined based on standard conditions such as at 1 atm, 298 K and in 1M solution. The potentials can

also be used to compare the strength of anodic or cathodic behavior of electrochemical reactions, qualitatively.

There are several concepts to be clarified for further understanding of the basics of the electrochemistry. One of the essential relations is Nernst equation which shows the mathematical relationship between the electrode potential and the concentration of species on the surface at equilibrium conditions. [26]



$$E = E^\circ - \frac{RT}{nF} \ln \frac{[Red]}{[Ox]} \quad (11)$$

When applied potential is more negative than the Nernstian potential, reduction process occurs, and the reductant gives electron to the electrolyte. The reduction reaction takes place in cathode side, i.e. backward reaction in equation (10). In contrast, when applied potential is more positive than the Nernstian potential, oxidation process occurs, and the oxidant gains electron. The oxidation reaction occurs in anode side, i.e. forward reaction in equation (10). The potential of an electrochemical cell is calculated from the subtraction of cathodic potential to anodic potential. [26]

$$E_{cell} = E_{cathode} - E_{anode} \quad (12)$$

It is important to emphasize that the concentration terms in the equation (11) refers to the ones on the bulk although there is a concentration gradient between the electrode surface and the bulk. For instance, in a reduction part in redox reaction, after applying potential to the electrode, the oxidizing agent amount approaches to zero on the surface while it increases as moving from electrode surface to the bulk solution until it reaches the same concentration with the bulk. This concentration gradient causes the diffusion and the layer where diffusion takes place is called as diffusion layer.

Butler-Volmer equation is one of the most importing equation in the electrochemistry which shows the mathematical relationship between current and potential. [26]

$$i = F A k^0 [C_o(0, t) e^{-\alpha f(E-E^0)} - C_R(0, t) e^{(1-\alpha)f(E-E^0)}] \quad (13)$$

Butler-Volmer model for electrode kinetic predicts that if one applies more positive potential than the equilibrium potential, the energy barrier for reaction to proceed shifts in favor of oxidation while more negative potential than the equilibrium potential contributes the shift towards reduction reaction. [26]

The general form of Butler-Volmer model in equation (13), both mass transport and kinetic terms are included. It means two different limitations included in the general forms. At small overpotentials, which is described as the difference of applied and standard potentials, charge transfer kinetics dominate the mass transport while mass transport limits the reaction at large overpotentials. The simplification at high overpotentials result in Tafel relation which expresses the logarithmic relation between the overpotential and the current. In other words, Tafel equation provides electrochemical kinetic inferences about the reaction rate and overpotential. There is a linear relation at high overpotentials above 118 mV. The Tafel relation is shown in the equation (14) and Figure 2.1. [26]

$$\eta = a + b \log i \quad (14)$$

$$a = \frac{2.3RT}{\alpha F} \log i_0 \quad (15)$$

$$b = \frac{-2.3RT}{\alpha F} \quad (16)$$

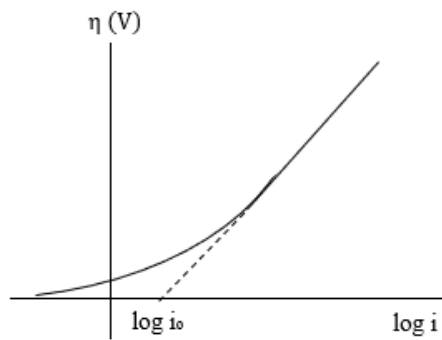


Figure 2.1 Tafel diagram η vs $\log i$

There are two factors limiting the faradaic current in electrochemical cell which are mass transport and kinetic limitations. Mass transport is known as the material transferred between the bulk and the electrode surface whereas charge transfer kinetic is the electron transfer at the interface. Mass transport in the electrochemical cell occurs in three different ways such as diffusion, migration and convection. Diffusion is the spontaneous movement of components from denser to less dense direction due to their concentration difference as a driving force. Migration is the movement of charged particles in the electrolyte due to electric field gradient. Convection is the movement of materials as a result of the hydrodynamic solution in the existence of flow regime, e.g. stirring the electrolyte.

If the fact that charge on the electrode surface is zero is supposed, ions near electrode surface migrate as a result of applied potential. These migrations originate not because of the electrochemical reaction occurring but from the surface charge which are unbalanced until the positive and negative charges reach an equilibrium. The accumulation of those charges forms the layer at the interface between the electrode surface and the bulk which is called electrical double layer. [26]

2.2 Electrochemical Activity Tests

2.2.1 Linear Sweep Voltammetry (LSV) and Cyclic Voltammetry (CV)

The any method that measures current-potential behavior is called as voltammetry. LSV is a basic voltammetry which measures the current produced in a fixed potential range at a constant sweep rate with a single scan. It measures one way of either anodic or cathodic current based on the voltage applied.

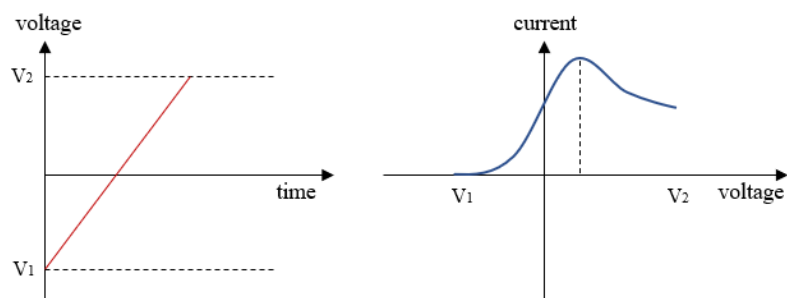


Figure 2.2 Potential and current behavior in LSV

The main parameter affecting the current obtained in addition to voltage applied is the scan rate. As it increases, the higher current is obtained. Also, LSV is a stagnant measurement where there is no contribution of convective mass transfer to the rate of reaction. Therefore, the effect of electrical double layer can be minimized only with the scan rate.

LSV is applied to C-Ag/Pt core/shell NPs to remove Ag from the core by means of dissolution of Ag^+ ions, formed as a result of the oxidation reaction of Ag, to the electrolyte for the modification of NPs via electrochemical leaching within the context of this project.

On the other hand, CV is a back-and-forth scan in the range of extreme positive and negative potentials. It basically is multiple LSV in sequence.

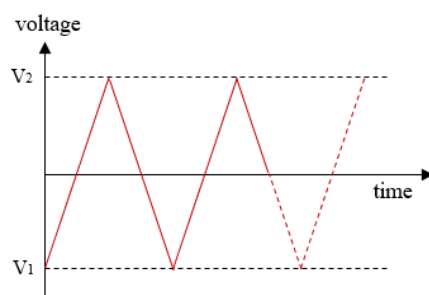


Figure 2.3 Potential profile as a function of time in CV

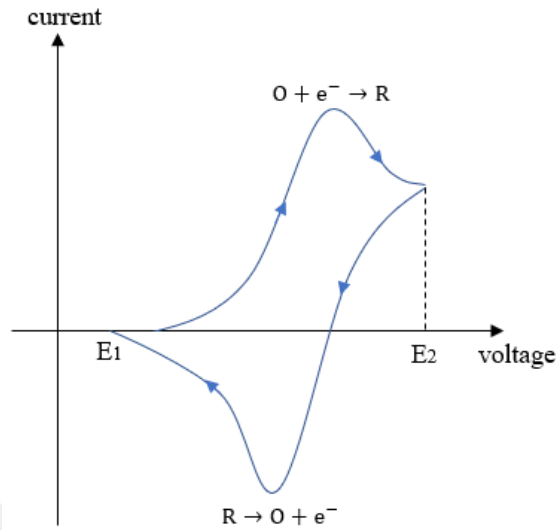


Figure 2.4 Current profile as a function of voltage in CV [26]

Since the mass transport does not occur with the convective mass transfer term, the scan rate can vary the activity. The relation between the maximum current obtained and the scan rate is shown in Randles-Sevcik equation in (17). [26]

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} v^{1/2} C_A \quad (17)$$

2.2.2 Rotating Disc Electrode (RDE)

Rotating disc electrode is a hydrodynamic method to measure current-potential diagram involving forced convection in addition to diffusion and migration to the mass transport where convection term dominates the others. The method is quite useful since it eliminates the electrical double layer which limits the reactions. Also, the rate reaction becomes fasten since the convective mass transfer is efficiency than diffusive mass transfer. The set-up basically contains a disc of electrode attached to a rod covered with insulating material such as Teflon. The rod directly connects with the motor which controls the rotation rate, i.e. angular velocity.



Figure 2.5 RDE Set-up

The velocity of the fluid, in this case the rotational speed, determines the flow type. If the flow is smooth, it is called as laminar flow while the unsteady and chaotic flow is called as turbulent flow. Reynolds number is used to determine the flow type whether it is laminar or turbulent. It is directly proportional with the velocity. If Reynolds number is less than a certain characteristic value, the flow is laminar whereas if it is greater than the value, the flow is turbulent.

$$\text{Re} = \frac{\omega r_1^2}{\nu} \quad (18)$$

When the disc rotates, the bulk near electrode rotates with it due to shear stress. Therefore, as a result of this motion, hydrodynamic layer, which is also stagnant layer, forms. The dominant mass transfer term is convection from bulk to electrode surface until reaching the stagnant layer. After the hydrodynamic layer, as getting close to electrode surface, diffusive mass transfer term becomes dominated. The very thin layer near the electrode surface in the stagnant layer where no convection exists, and mass transfer occurs only via diffusion is called as diffusion layer. The layer depends on the rotation speed and the kinematic viscosity of the fluid.

RDE system is based the simultaneous calculations of both convective and diffusive equations. Therefore, the first important equation derived from the current as a surface flux is Levich equation given in equation (19).

$$i_{L,c} = 0.62nFAD_0^{2/3}\nu^{-1/6}\omega^{1/2}C_0 \quad (19)$$

$$i_{L,c} = nFam_0C_0 \quad (20)$$

Mass transfer coefficient, m_0 , is the ratio of diffusivity coefficient and diffusion layer. Therefore, by rearranging the equations, the relation for diffusion layer thickness is found in equation (21). [26]

$$\delta_0 = 1.61D_0^{1/3}\omega^{-1/2}\nu^{1/6} \quad (21)$$

The Levich equation in (19) presents linear relationship between limiting current and the square root of rotational speed. However, in slow kinetics, the equation brings a bias with a deviation near kinetic limitation conditions. Therefore, after rearranging the equation (19) by including the effect of kinetics without the mass transfer effects Koutecky-Levich equation is obtained.

$$\frac{1}{i} = \frac{1}{i_K} + \left(\frac{1}{0.620nFAD_O^{2/3} \nu^{-1/6} C_{O_0}} \right) \omega^{-1/2} \quad (22)$$

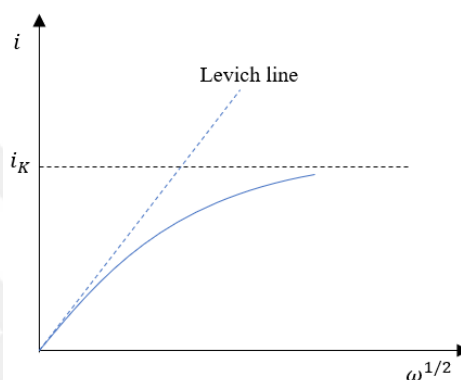


Figure 2. 6 Current vs square root of rotation speed graph in slow kinetics [26]

2.2.3 Electrochemical Analysis

In the project, electrochemical analysis was made mainly by RDE although CV and LSV were also used.

For electrochemical measurements, the ink was prepared from the obtained carbon supported catalysts to liquify the related powder sample. 1.5 mg catalyst was mixed with 0.2 mL of isopropyl alcohol and water mixture (1:1 by volume) via sonication for at least 30 min. 10 μ L from prepared ink was dropped on the glassy carbon electrode and let it to dry. After drying, 0.5 μ L of 0.05wt% Nafion solution was added at the top of the dried ink. The resultant catalyst amount on the electrode was 382 μ g/cm². Reference samples used are Vulcan XC72R and commercial 20wt% C-Pt.

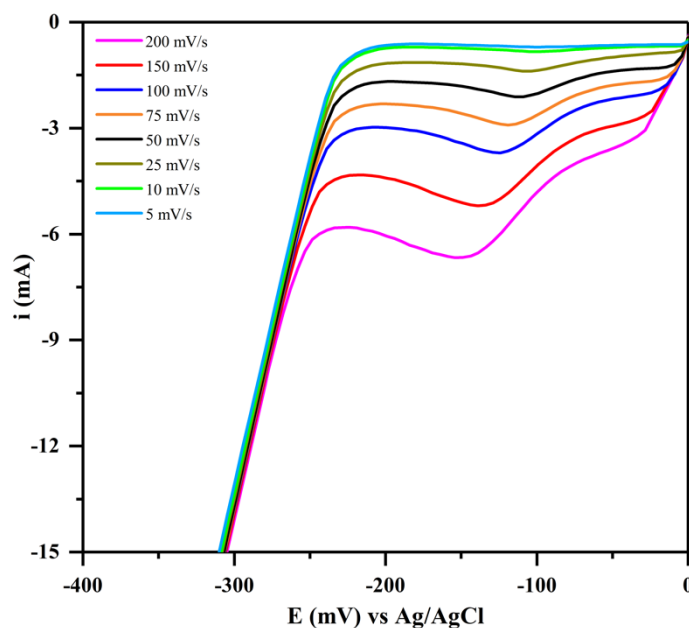


Figure 2.7 HER for commercial 20% C-Pt in 0.5 M H_2SO_4 at 1600 rpm with varying scan rates (mV/s) in RDE

Since the reaction is kinetically limited, as scan rates increase onset potential at each scan rates. The reason is because there is not enough time for each component. As the residence time decreases, the possibility of reaction to occur reduces.

The reason for the curvature behavior with increasing scan rate is due to the effect of capacitance which is directly proportional with the scan rate. Also, the thickness of the diffusion layer becomes shorter as scan rate increases.

Three electrode system was used for all electrochemical activity tests. Pt wire was used as a counter electrode while all measurements were based on Ag/AgCl as a reference electrode.

All activity tests in RDE for HER were performed at 1600 rpm and 5 mV/s in 0.5 M H_2SO_4 solution while they were at 1000 rpm and 5 mV/s in 0.1 M KOH solution for ORR. Also, CV measurements were performed in 0.1 M KOH and O_2 bubbling with 5 mV/s as scan rates.

2.3 Characterization Techniques

2.3.1 UV-Visible Spectrophotometer (UV-Vis)

UV-Visible Spectroscopy is a device that uses ultraviolet and visible light as an electromagnetic spectrum to detect the transmission, absorption and reflection properties of a material as a function of wavelength. The absorbed light by the material excites the electron which jumps from ground state to higher energy state as a result of the excitation. The theory of UV-Vis spectrophotometer is based on Beer-Lambert law in the equation (23). [27]

$$A = \log \left(\frac{I_0}{I} \right) = \epsilon Cl \quad (23)$$

It indicates that the amount of absorbed light by the solution is directly proportional the concentration of the analyte. Therefore, UV-Vis can be used for concentration determination from the absorber ions as well as the indication of the type of the absorber from the related peak positions.

Pure Ag NP has surface plasmon resonance peak around 400 nm. The shape and the exact value depend on the particles size. For alloy type bimetallic NPs, surface plasmon peak shifts between the peak value of constituents based on the change in composition and the distribution of the atoms. However, for core-shell type of bimetallic NPs, it depends on the thickness of the shell as well [28].

UV-Vis measurement within the context of the project was done for two main reasons: (i) to observe the surface plasmon resonance peak for pure Ag NPs and (ii) to make sure about the surface coverage of Ag for Ag/Pt core/shell NPs. For this purpose, the suspension of Ag and Ag/Pt were used. They were diluted with hexane and analytic hexane was used as a reference and baseline was drawn accordingly. The device used is “Shimadzu UV-3600 – UV-Vis-NIR Spectrophotometer” in KUYTAM.

2.3.2 Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

Mass spectrometry is an analysis technique measuring the amount of ionized components in the solution based on their mass to charge ratio. ICP-MS is a type of mass spectrometry which detects the amount of metals and nonmetals in the solution. It is a basic technique for elemental analysis having an ability to detect low concentrations even in the order of part per billion (ppb). In ICP-MS, inductively couple plasma is used to ionize the sample while mass spectroscopy is for detecting and quantifying the elements. [29]

The key point for reliable measurement in ICP-MS is the total dissolution of the desired component. For this purpose, microwave digestion method is used for elements hard to dissolve in room temperature.

ICP-MS measurement within the context of the project was used for the determination of metal composition in the catalyst. For this purpose, microwave digestion method was used. For this purpose, 2-3 mg of related catalysts were added into 8 mL of HNO₃ (90%, Sigma Aldrich) for Ag determination while they were mixed with 8 mL of aqua regia for Pt determination. Then, they were put into in closed vessel in the microwave oven for heating at 15 min to 200 °C and holding at 200 °C for 10 min. The resultant was filtered with syringe filter to remove unsolved carbon particles. For the ICP-MS, the samples prepared for Ag determination are diluted 10 times while no dilution was implemented to the ones for Pt determination [30].

The devices used in this project are “StartD Milestone Microwave Digestion” for microwave digestion in KUYTAM and “Agilent 7700x ICP-MS” for ICP-MS analysis in TÜPRAŞ.

2.3.3 Thermal Gravimetric Analysis (TGA)

TGA technique measures the change in weight of the sample as a function of temperature or time in isothermal conditions in the nitrogen, air and other certain gas atmosphere. Samples with powder form are used in the instrument. Platinum pan is used as a sample holder since it has nonporous structure and it is easy to clean.

TGA gives the information about the decomposition temperature of constituents in the material and the composition of components as a result of complete burning of desired species.

In the context of this project, TGA is used to determine the support percentage of the catalysts by burning the support material, i.e. Vulcan XC72R. It is done for ~5 mg of sample with a constant heating rate of 10°C/min from room temperature up to 800°C under nitrogen with flow rate of 40 mL/min and dry air with flow rate of 60 mL/min atmosphere. After the related measurement, TGA analysis were done based on the percent weight loss in the sample. The device used is “TGA Q500” in KUTEM.

2.3.4 X-Ray Photoelectron Spectroscopy (XPS)

XPS is a surface analysis technique that measures the kinetic energy of ejected electrons released from the material as a result of irradiation of X-ray light. It is a characterization technique providing the quantitative surface information such as elements in the surface, their oxidation states and molecular information by showing the chemical bonds in the related environment by using the fact that each electron ejected in different orbitals has a unique binding energy in a certain element. [31]

In briefly, the electron releases when incident x-ray beam hits the electron. The ejected electron is called as photoelectron. Another electron from higher energy state falls into the core level to fill the vacancy of released photoelectron. As a result, Auger electron is released to conserve the energy. The simple pathway of related XPS mechanism is shown in Figure 2.8.

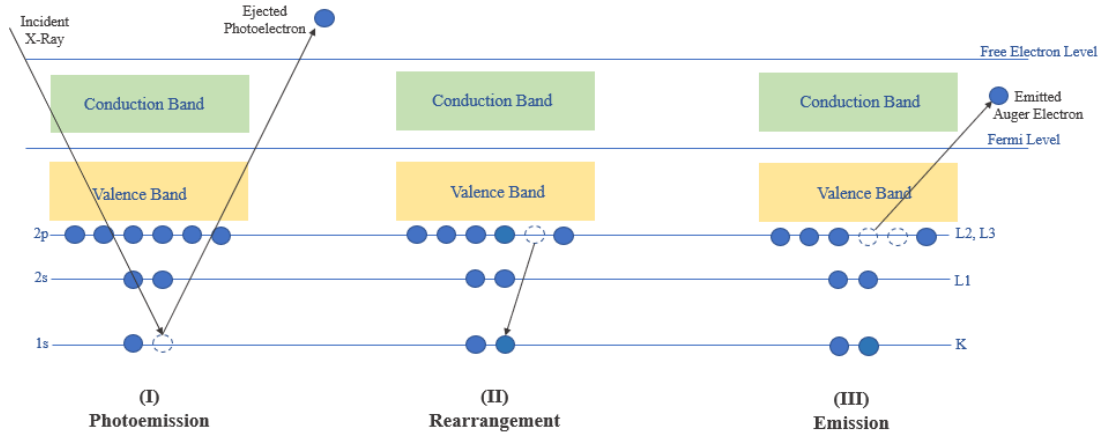


Figure 2.8 Schematic of XPS pathway

XPS measures kinetic energies of all ejected electrons including both photoelectron and auger electron. While the kinetic energy of photoelectron depends on the energy of incident beam, the energy of auger electron does not. Therefore, the peak position of auger electron does not change with the energy source and no shift is observed with different beam source such as Al K alpha or Mg K alpha. The peaks of photoelectron are generally narrower compared to the peaks of auger electron. By using these two basic facts, peaks can be easily distinguished.

The equation (24) shows the main relation that XPS uses for the determination of kinetic energy of photoelectron. [32]

$$h\nu = E_B + E_K + \phi \quad (24)$$

Sampling depth is the depth of majority ejected photoelectrons (approximately 99%) that reach the surface.

$$I_s = I_0 e^{(-d/\lambda \cos \theta)} \quad (25)$$

The depth of surface that XPS can detect is 2-10 nm for Al K alpha [33]. Hence, it can be easily concluded that XPS analysis is highly surface sensitive. It does not give the idea about bulk properties such as bulk compositions. Also, surface contamination affects the measurement.

The main information is obtained from peak shifts in XPS. Peak shifts show the change in oxidation state since the interaction with atoms via chemical bonds and neighbors alters the binding energy of the photoelectron. In other words, different bonds with different elements causes peak shift due to change in kinetic energy of photoelectron. For instance, C1s peak due to C-C bond in hydrocarbon group is at 284.5 eV while it is at 288.0 eV for C=O bond in carbonyl group [34].

For XPS measurement within the context of the project, following steps were applied during the analysis of the results:

- i. Binding energy correction was done based on C1s by assuming that it has a peak at 284.5 eV.
- ii. In order to be able to compare each XPS results, intensity values were divided by number of scans for individual measurements.

The devices used in this project is “Thermo K-Alpha X-Ray Photoelectron Spectrometer” in KUYTAM.

2.3.5 X-Ray Powder Diffraction (XRD)

XRD is a technique for identification of crystalline structure of materials such as interplanar distances of atoms, orientation of atoms or grains and detection of unknown sample from certain crystalline structure. The basic mechanism is based on Bragg’s law in equation (26).

$$n\lambda = 2d\sin\theta \quad (26)$$

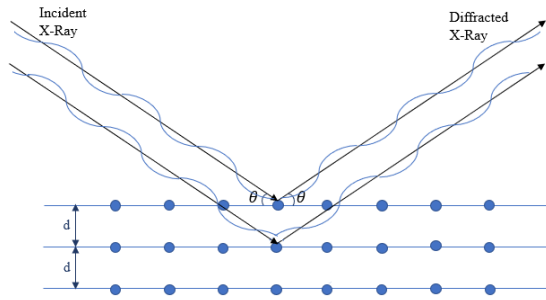


Figure 2.9 Schematic representation
of Bragg's Law

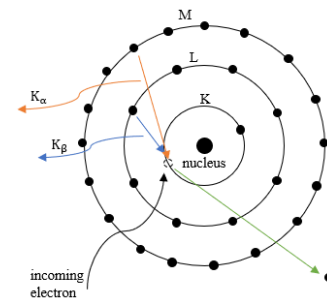


Figure 2.10 X-Ray emission
in Bohr atom model

XRD simply consists of X-Ray tubes, sample holder and the detector. In X-Ray tubes, there are two types of radiation generated such as characteristic radiation and bremsstrahlung radiation. Characteristic X-Ray radiation is generated from the interaction between electron shells. More specifically, it is the energy loss of photon released from the higher shell to fill the hole, which forms due to electron released by incident photon, in lower shell. Bremsstrahlung X-Ray radiation is generated from the interaction in atomic radius. More specifically, it is the energy loss of electrons due to the descending acceleration. Electrons pass close to a nucleus and slow down due to the attractive force from the nucleus. By changing the angle of sample and detector with goniometer, constructive interference of waves is recorded when they apply Bragg's Law. [35]

The device used in this project is "Bruker D8 Advance X-Ray Diffractometer" in KUYTAM.

2.3.6 Electrochemical Active Surface Area (ECSA)

The determination of electrochemical active surface area has huge importance to understand the electrochemical reactivity. Thus, it should be specified since the area of the electrode doesn't show the real active area where reactions take place. As indicated in Randles-Sevcik equation in (17), the square root of scan rate is directly proportional to the maximum current obtained in CV analysis. Therefore, after choosing proper method with a certain electrochemical reaction, CV graphs were drawn to determine the peak currents by varying scan rates. The reaction for chosen method is the ferrocene reduction reaction. The electrolyte was aqueous solution of 0.01 M $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.1 M Na_2SO_4 mixture. Na_2SO_4 was added to increase the ionic conductivity of the electrolyte. The related reaction was written below. [26]



The slope of peak current vs square root of scan rate graph is directly proportional with the electrochemical active surface area. Hence, in order to compare ECSA of prepared catalysts, the slopes of related plot were compared within the context of the project without needing any further calculation for exact value.

CHAPTER 3

SYNTHESIS AND CHARACTERIZATION Ag/Pt CORE/SHELL NANOPARTICLES and THEIR ASSEMBLY ON CARBON SUPPORT

3.1 Literature Review

Core/shell NPs promise wide range in electrocatalyst' field. Various combinations with different metals have been studied. Core/shell NPs containing Ag and Pt have been investigated from literature.

M. Liu et. al. synthesized carbon supported Pt-Ag alloys, hollow alloy and Ag/Pt core/shell NPs by galvanic replacement reaction for ORR. They achieved the enhancement in ORR activity due to ligand effect and the downshift in d-band center to the interaction between Pt and Ag [36].

A. Londono-Calderon et. al. evaluated Au-Ag-Pt trimetallic NPs synthesized via chemical reduction method and Au/AgPt yolk-shell nanocubes via galvanic replacement reaction for HER. Au/AgPt yolk-shell structures show significant improvement in HER activity such as -20 mV vs NHE as an overpotential to reach -10 mA/cm² as a current density while Au-Ag-Pt trimetallic nanocubes indicate slow reaction rate such as -250 mV vs NHE as an overpotential to reach -10 mA/cm². The results clearly demonstrate that the existence of the synergic effect between Ag and Pt enhances electrocatalytic activity of Pt for HER [37].

C. Li and Y. Yamauchi suggested the synthesis of Ag/Pt core/shell NPs with dendritic Pt shells without using ionic surfactant, P123, and applied the NPs for methanol oxidation reaction. They showed that although the synergetic effect between the shell

and the core has an importance on the structure, the thickness of the dendritic Pt as a shell supplies highly electrochemical active surface area which enhances the activity [38].

L. Chen and co-workers studied with the characterization of water-soluble Ag/Pt core/shell NPs with different Pt shell thickness synthesized by seed-growth method mainly in UV-Vis spectra. They observed the changes in the surface plasmon peak position and broadening by varying the compositions and particle sizes. They observed the red shift in bimetallic NPs as Pt composition increases; however, when the composition of Ag decreases below 50% in the structure, the blue shift occurs which shows the importance of composition in the core/shell NPs [39].

Z. Peng and co-workers studied with Pt-on-Ag NPs by changing the reaction conditions such as temperature and the duration. They investigated the importance of these parameters on Pt growth on Ag atoms. They also observed promising ORR activity with Pt-on-Ag NPs [40].

3.2 Synthesis of C-Ag/Pt Core/Shell Nanoparticles

La Mer and coworkers were extensively studied on the mechanism of the formation of colloids or nanocrystals in solution [41] [42]. According to the La-Mer theory, the controlled and separated nucleation and growth processes in which a burst nucleation of metal ions should be followed by an initially rapid and then slow growth process is desired to yield monodisperse metal NPs. Among the synthesis protocols reported in the literature, the surfactant-assisted solvothermal protocol provides the desired conditions for the synthesis of monodisperse metal NPs [43]. Therefore, we selected this route to synthesized Ag/Pt core/shell NPs. For the synthesis of Ag/Pt core/shell NPs, a seeded-growth method was used. In our synthesis protocol, firstly, monodisperse Ag NPs were synthesized as seeds and then Pt NPs were grown on the Ag seeds as a thin layer. In a typical synthesis of Ag NPs as seeds, silver(I) acetate was dissolved in the mixture of oleyl amine (OAm), oleic acid (OAc) and 1-octadecene

(ODE) in a four-necked glass reactor (Figure 3.1). The resultant mixture was heated under argon gas flow. In the protocol, OAm served as both surfactant and the reducing agent OAc functioned as a co-surfactant and ODE was used as an organic solvent. Next, for the formation of a thin layer of Pt NPs, as-synthesized Ag NPs were dispersed in the mixture of OAm and OAc. In this recipe, OAm has triple function as solvent, surfactant and solvent while the role of oleic acid was co-surfactant again.



Figure 3.1 Synthesis setup

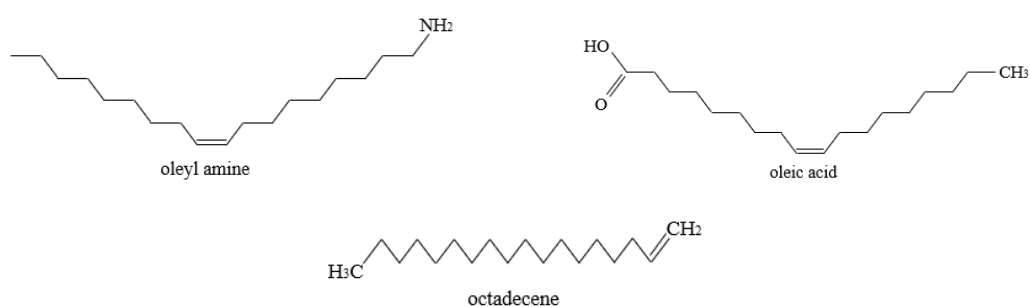


Figure 3.2 Structures of octadecene, oleic acid and oleyl amine

3.2.1 The recipe for the synthesis of monodisperse Ag Nanoparticles

For a typical Ag NPs synthesis, 1 mmol silver acetate (99%, Sigma-Aldrich) was added into the ODE, OAm and OAc mixture (10:1:1 by volume) in the reactor.

Temperature rise was adjusted in a controlled manner up to 60°C, first. After 10 min at 60°C to obtain enough homogeneity, temperature was increased up to 180°C, slowly. The color turned to reddish brown as expected in Figure 3.3. 30 min later, the reactor was cooled down to room temperature. Mixture of isopropyl alcohol and acetone was added to the reactor. The centrifuge was performed at 8500 rpm for 12 min. After discarding the decantation, the residue was taken with hexane. The resultant was Ag NPs suspension with hexane. The reaction was fulfilled in dark environment with argon flow.



Figure 3.3 Synthesis of the suspension of Ag NPs whose color is reddish brown

3.2.2 The recipe for the synthesis of Ag/Pt core/shell nanoparticles

After having Ag NPs, Ag seeds were coated with Pt NPs to obtain Ag/Pt core/shell NPs. For three different composition, 25, 35 and 45 mg of PtCl_2 was dissolved in 10 mL oleyl amine with sonication at around 45°C. Meanwhile, density calculation was done to determine the Ag suspension amount added to the reaction. For this purpose, 0.1 mL of Ag suspension was placed into a vial and hexane was evaporated with the help of nitrogen flow. From the weight of the residue, the density of Ag NPs was calculated. After dissolution of PtCl_2 in oleyl amine, 1 mL of oleic acid was added to the reactor. 21 mg of Ag suspension was added dropwise to the mixture. The reaction temperature was increased up to 60°C. After staying at this temperature for 15 min, it

was raised to 220°C with a constant heating rate of ~4°C/min. After 30 min as a waiting period at 220°C, the reactor was cooled down to 50°C. Then, analytic ethanol was added to the mixture in the reactor. The centrifuge was performed at 8500 rpm for 12 min. After discarding the decantation, the residue was obtained by pouring analytic hexane. At the end, the resultant was Ag/Pt core/shell NPs suspension with hexane. The reaction was performed in argon environment.

3.2.3 Supporting Ag/Pt core/shell nanoparticles on carbon black

Ultrasonic bath was used to mix Vulcan XC72R and hexane for 15 minutes. The required amount of Ag/Pt core/shell NP suspension, which was adjusted based on 20 wt.% catalyst supported on carbon black, was added dropwise to that mixture. The sonication continued for 2 hours in total at room temperature. Then, the centrifuge at 7000 rpm for 12 min was performed after the addition of analytic ethanol to the related mixture. The decantation was discarded, and the residue was dried under vacuum by using the rotary evaporator. Obtained resultant was carbon supported Ag/Pt nanocatalysts.

For references, 20wt% Pt on carbon and bare Vulcan XC72R were used for all analysis.

25 mg PtCl₂ (or 35 and 45 mg PtCl₂) written after C-Ag/Pt between the parenthesis refer to the initial Pt precursor added to the sample during synthesis to indicate the variations of Pt content in the catalysts. This notation will be used throughout the thesis.

3.3 Characterization for C-Ag/Pt Core/Shell Nanoparticles containing different amount of Pt

3.3.1 UV-Vis Analysis for C-Ag/Pt core/shell determination

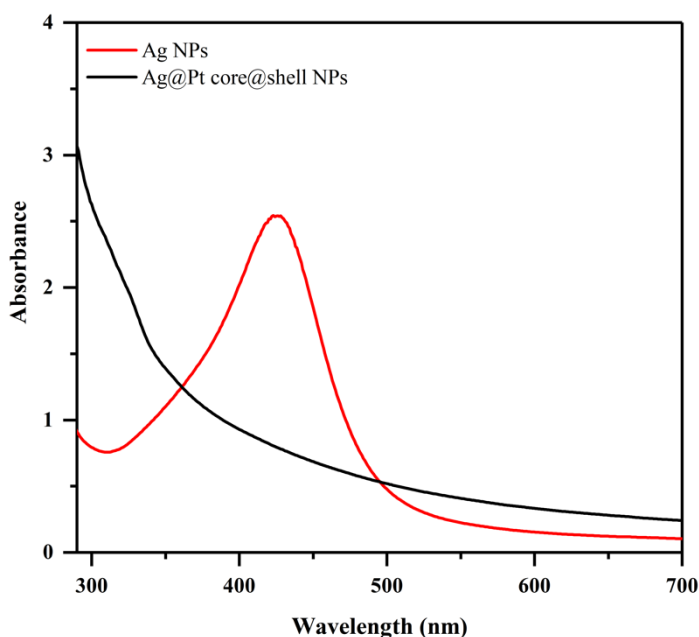


Figure 3.4 UV-Vis for Ag and Ag/Pt core/shell NPs

UV-Vis spectra of Ag and Ag/Pt core/shell NPs is presented in Figure 3.4. Since Ag NPs show characteristics surface plasmon resonance peak (SPR), UV-vis absorption spectra give an idea about the surface state of Ag NPs [38]. As seen by Figure 3.4, the SPR peak of Ag NPs at ca. 420 nm disappears for Ag/Pt core/shell NPs. It reveals that Ag surface was covered by Pt atoms. It can be assumed that the surface coverage of Ag occurred both due to oleyl amine as a surfactant and Pt as a shell and thereby, they are referred to Ag/Pt core/shell NPs by opening a parenthesis at this point and leaving the further proof to TEM section to close it.

3.3.2 ICP-MS Analysis for composition determination

Table 3.1 ICP-MS Results

Samples	Pt (wt%)	Ag (wt%)
commercial C-Pt	18.8	-
Ag-C	-	4.5
C-Ag/Pt (25 mg PtCl ₂)	9.5	3.1
C-Ag/Pt (35 mg PtCl ₂)	10.5	2.9
C-Ag/Pt (45 mg PtCl ₂)	18.4	3.0

The compositions of C-Ag/Pt nanocatalysts were analyzed by ICP-MS and the results are depicted in Table 3.1. The mass percent of Pt in commercial C-Pt (20 wt% Pt) catalysts was found as 18.8 wt% which is an acceptable value compared to the theoretical one. The Pt content of C-Ag/Pt catalysts with different shell-thicknesses was found to be 9.5, 10.5 and 18.4 wt% for the synthesis in which 25, 35 and 45 mg PtCl₂ was used, respectively. The incremental increase of Pt content for C-Ag/Pt from 25 mg PtCl₂ to 45 mg PtCl₂ is convenient even though there is no linear relationship between them. These results indicate that C-Ag/Pt (25 mg and 35 mg PtCl₂) contain less Pt than commercial C-Pt, even approximately half amount of commercial sample, while the amount of Pt in C-Ag/Pt (45 mg PtCl₂) is close to commercial C-Pt.

The initial amounts of Ag added during the synthesis were the same for all C-Ag/Pt. Therefore, the results that weight percent of Ag are around 3% for all C-Ag/Pt nanocatalysts are consistent with each other. However, the reason why the amount is lower than expected is due to the assumption that the amount of Ag and organics, e.g. OAm and OAc, are the same in the suspension added to the reactor during Ag/Pt core/shell NPs synthesis. Apparently, the compositions of organics are higher than Ag in the Ag NPs suspension.

3.3.3 TGA Analysis for the carbon percentage determination

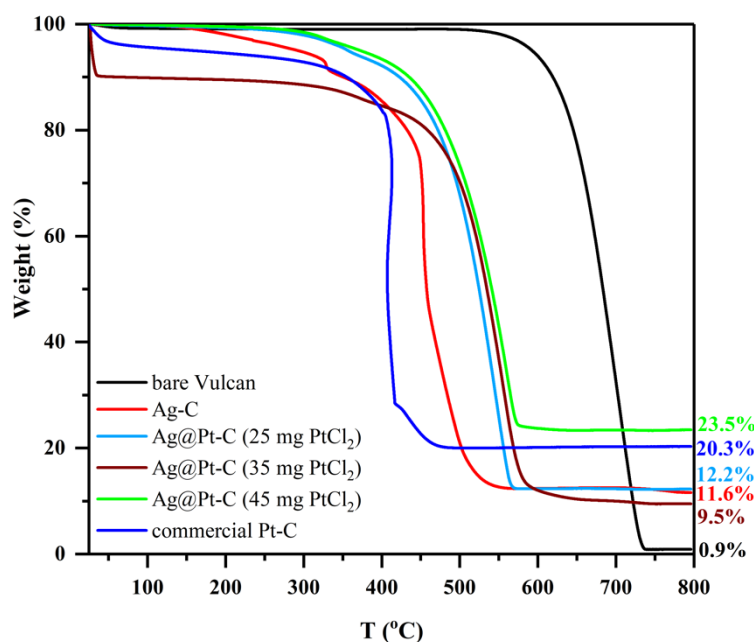


Figure 3.5 TGA graph for bare Vulcan, C-Ag/Pt (25, 35 and 45 mg PtCl₂) and commercial C-Pt

The metal content of the C-Ag/Pt catalysts were further verified by TGA analysis. As can be seen by the TGA profile in Figure 3.5, the amount of carbon support for C-Ag/Pt catalysts are different than expected. There is no linearity between the carbon content of the samples even if they were prepared exactly same recipe with same amounts. VulcanXC72R was analyzed in TGA as a reference sample. The oxidation of carbon black requires high temperature starting from approximately 550°C. Lower temperatures in the presence of metal NPs could be attributed to their catalytic role in the combustion process due to catalytic effect of metals that eases the combustion process. All of C-Ag/Pt (25, 35 and 45 mg PtCl₂) catalysts show same trend in TGA. Their curves are flat until around 300°C and continue with sharp decrease starting from 400°C until 580°C. The former trend shows the decomposition of organic materials such as oleyl amine while the latter one is where carbon burnt. The indicated curve

trend is more obvious for C-Ag. Although the temperature where organic components started to evaporate is same with core/shell samples, carbon started to burn earlier. The reason is the weaker metal-carbon bond in monometallic materials compared to core/shell samples which contains bimetallic compounds. Commercial C-Pt has some impurities whose decomposition temperature starts from 400°C. According to TGA result, commercial C-Pt contains 20.3% of Pt as expected while C-Ag has 11.6% of Ag after carbon burn off. The result is not exactly parallel with ICP-MS result for C-Ag since pure Ag NPs may be oxidized while carbon was burning. Therefore, the remaining amount may not only be Ag but also Ag₂O, the most favorable oxide phase of Ag, which makes sense when taking into consideration of the comparison between the difference of molecular weight ratios ($\text{Ag}_2\text{O}:\text{Ag} \cong 2$) and the difference in results of ICP-MS and TGA (~2.5 times lower Ag amount in ICP-MS). On the other hand, the order of metal composition for core/shell samples are 23.5%, 12.2% and 9.5% for C-Ag/Pt (45 mg PtCl₂), C-Ag/Pt (25 mg PtCl₂) and C-Ag/Pt (35 mg PtCl₂), respectively, which are consistent with ICP-MS results. Both results show that C-Ag/Pt (25 mg and 35 mg PtCl₂) samples contain less Pt than commercial C-Pt while C-Ag/Pt₄₅ includes more metal than even commercial C-Pt.

3.3.4 Surface Characterization done by XPS for C-Ag/Pt core/shell nanoparticles with varying Pt amount

In Figure 3.6, Pt 4f and Ag 3d XPS spectra are shown for C-Ag/Pt catalysts containing different amount of Pt. Pt 4f XPS spectra shows that Pt content in the surface of the catalysts decreases from C-Ag/Pt (45 mg PtCl₂) to C-Ag/Pt (25 mg PtCl₂) as expected based on peak intensities. Moreover, the binding energies tabulated in the Table 3.2 indicate that all samples have 4f_{7/2} peak at ~71.2 eV which is attributed to the existence of metallic Pt [44]. In addition, 4f_{5/2} peak to 4f_{7/2} peak ratio was calculated as 0.72 for single crystalline Pt(111) as a reference sample (Appendix II). Pt 4f spectra in Figure 3.6 demonstrates that the related peak ratios are 0.90, 0.81, 0.83 and 0.83 for commercial C-Pt, C-Ag/Pt (25, 35 and 45 mg PtCl₂), respectively, (see Appendix II

for the details of the peak fitting). Therefore, C-Ag/Pt (25 mg PtCl₂) is closer to metallic Pt compared to others based on these calculated peak ratios. There are shoulders at the higher binding energy sides for 4f_{5/2} and 4f_{7/2} lines particularly in the commercial C-Pt which can be attributed to oxide formation. The shoulder at higher binding energy side of 4f_{7/2} particularly for commercial C-Pt originates from the hidden peak of PtO₂ at 74.1 eV which is also consistent of the O 1s peak at 531.8 eV in Figure 3.7 [45]. The fact that the peak to peak ratio of 0.90 as commercial sample is quite higher than the reference Pt(111) as 0.72 is another representation of high amount of oxide formation. Furthermore, the analysis of the peak broadening seen in the C-Ag/Pt samples indicates that there is not only Pt⁰ in the surface of the structure but also other oxidation states of Pt such as 2+ in the form of PtO exist due to peaks at ~72.4 eV contributing to 4f_{7/2} [46]. Consequently, the reasons of peak broadening and high peak to peak ratio is because of oxide formation in the surface.

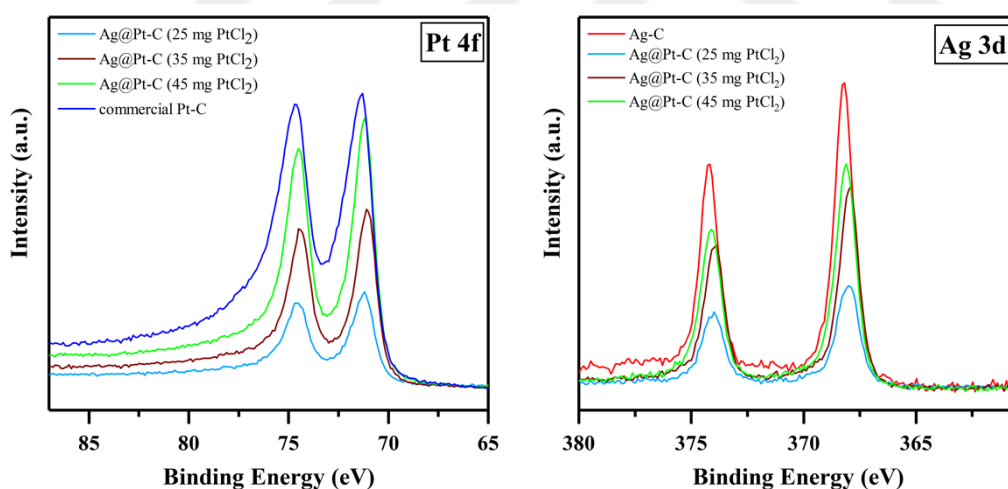


Figure 3.6 XPS Pt 4f and Ag 3d graphs for C-Ag/Pt (25, 35 and 45 mg PtCl₂) core/shell NPs

In Figure 3.6 Ag 3d XPS spectra, the vertical axis of C-Ag was scaled down with the multiplication of 0.05 for proper view since the intensity of C-Ag much higher than

core/shell NPs. By taking this minimization into account, direct comparison for peak intensities can be considered which indicates that Ag content decreases from C-Ag/Pt (45 mg PtCl₂) to C-Ag/Pt (25 mg PtCl₂). Although the highest amount of Ag is in Ag-C is confirmed from ICP-MS results in Table 3.1, the correlation between core/shell NPs is incoherent with the same table since the initial amount of Pt added are same for all three samples. However, this situation can be explained from the variations of particle size and distributions in the samples as explained in TEM section. Also, the number density in the measured samples could be different due to the inhomogeneity between the carbon support and metals in the samples.

Table 3.2 XPS peaks of Pt 4f and Ag 3d for C-Ag/Pt core/shell NPs in Figure 3.6

Samples	Pt 4f (eV)		Ag 3d (eV)	
	4f _{5/2}	4f _{7/2}	3d _{3/2}	3d _{5/2}
C-Ag	-	-	374.2	368.2
C-Ag/Pt (25 mg PtCl ₂)	74.6	71.2	374.0	368.0
C-Ag/Pt (35 mg PtCl ₂)	74.5	71.1	373.9	368.9
C-Ag/Pt (45 mg PtCl ₂)	74.5	71.2	374.1	368.1
commercial C-Pt	74.7	71.3	-	-

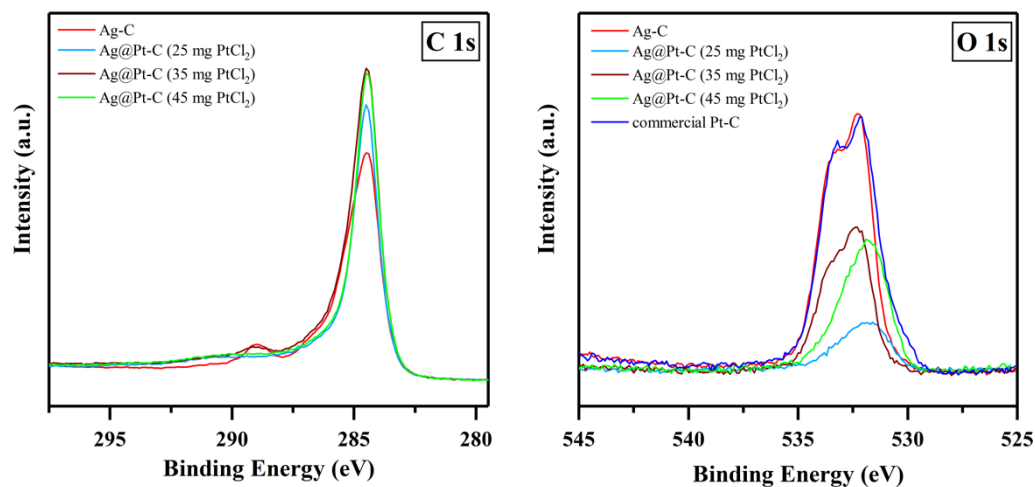


Figure 3.7 XPS C 1s and O 1s graphs for C-Ag/Pt (25, 35 and 45 mg PtCl₂) core/shell NPs

C 1s and O 1s XPS spectra are shown in Figure 3.7 for C-Ag/Pt NPs containing different amount of Pt. The alignment in C 1s peaks at 284.5 eV is due to binding energy correction [44]. The C-O bond explains the reason why the peak in high binding energy side of C 1s peak of Ag-C did not overlap with others as in the lower binding energy side. Therefore, the peak at ~288.5 eV for Ag-C and C-Ag/Pt (35 mg PtCl₂) can be assigned to C=O and C-O bonds. O 1s peaks at 533.4 eV and shoulders at ~531.8 eV for same samples also confirm the existence of the related species [34]. In addition, the O1s peaks at 531 eV can be associated with the oxygenated metal species. The C 1s XPS peak at ~290 eV for C-Ag/Pt (25 mg PtCl₂) and (45 mg PtCl₂) can be attributed to O-C=O group [47]. Consequently, C 1s and O 1s XPS peaks not only show the oxygenated species in the catalysts but also highlighted the existence of contaminations in the samples.

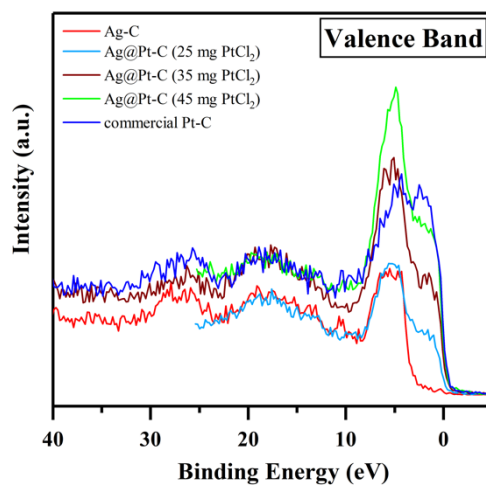


Figure 3.8 XPS Valence Band graph for C-Ag/Pt (25, 35 and 45 mg PtCl₂) core/shell NPs

Valence band XPS spectra is shown for C-Ag/Pt NPs in Figure 3.8. Ag 4d_{5/2} peak is at ~5 eV [48]. Therefore, no other peak is observed as approaching to Fermi level for Ag-C. On the other hand, for commercial Pt-C, there are two peaks around 3 and 5 eV characteristic to Pt 5d states. By comparing Ag-C and commercial Pt-C spectra, it can be concluded that the sharper peak around 5 eV for C-Ag/Pt NPs have Ag characteristics more than Pt while the shoulder in lower binding energy side which is near Fermi level as around 2 eV is due to Pt contribution. For instance, Ag content in C-Ag/Pt (45 mg PtCl₂) with sharper peak around 5 eV is highest compared to others while order continues with C-Ag/Pt (35 mg PtCl₂) and C-Ag/Pt (25 mg PtCl₂) which are consistent with XPS Ag 3d spectra in Figure 3.5. Consequently, it can be concluded that initial Ag amounts near surface are different for C-Ag/Pt NPs with different Pt content.

3.3.5 Structural Characterization by XRD

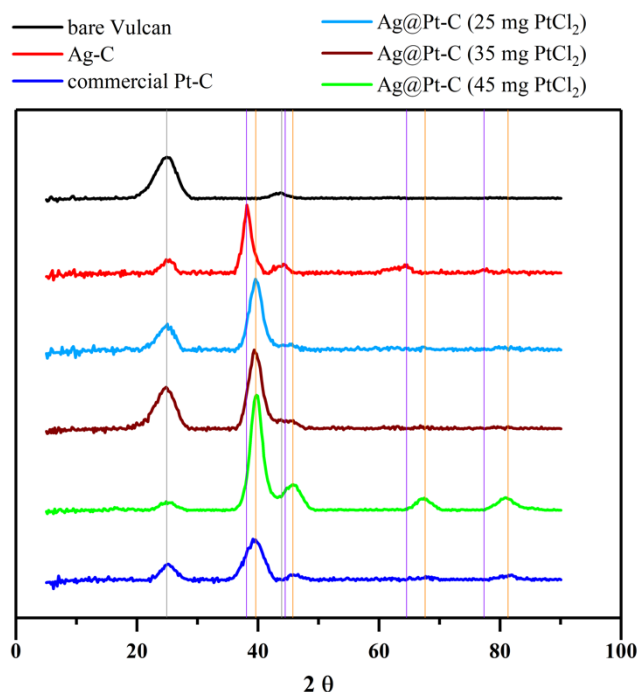


Figure 3.9 XRD for core-shell NPs

In the XRD data for core-shell NPs presented in Figure 3.9, gray, purple and orange lines represent 2θ peak positions for pure C, Ag and Pt, respectively (see Appendix III for related values). Data for all curves were multiplied by a certain value in order to place them into one graph, separately. Therefore, direct comparison from peak intensity values would not be correct. All samples have C (002) peak at 24.8° due to carbon support. According to Figure 3.9, Ag-C has all Ag peaks originated from the diffraction from (111), (200), (220), and (311) planes; however, core-shell NPs do not have same Ag peaks. There are also peak shifts in core-shell NPs compared to pure C-Ag between 38-40 eV. Therefore, some amount of Pt NPs may diffuse to Ag NPs in the core and form alloy structure. In other words, the reason why no Ag peaks in core-shell may be because there is no pure Ag in the core, but alloy formation occurs in the core and changes the lattice parameters of Ag.

3.3.6 Microscopic Characterization including Imaging and Quantitative Analysis by using TEM and EDX

Figure 3.10 shows the particle distribution of C-Ag/Pt (25 mg PtCl₂) NPs in 50 nm as a scale bar in TEM dark field mode. It is clearly seen that the number density, number of particles per unit area, of the sample is high based on Figure 3.10. Therefore, it indicates that the dispersion of the NPs during sample preparation is not good enough for homogeneous distribution. In addition, particle size distribution is quite varied. Thus, particles of C-Ag/Pt (25 mg PtCl₂) are not monodispersed according to Figure 3.10. Average particle size of C-Ag/Pt (25 mg PtCl₂) core-shell NPs is ~7.4 nm.

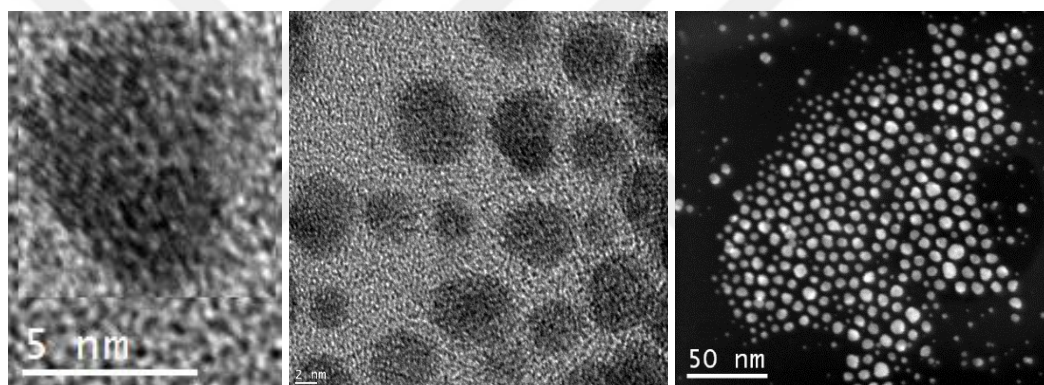


Figure 3.10 Particle distribution of C-Ag/Pt (25 mg PtCl₂) in TEM

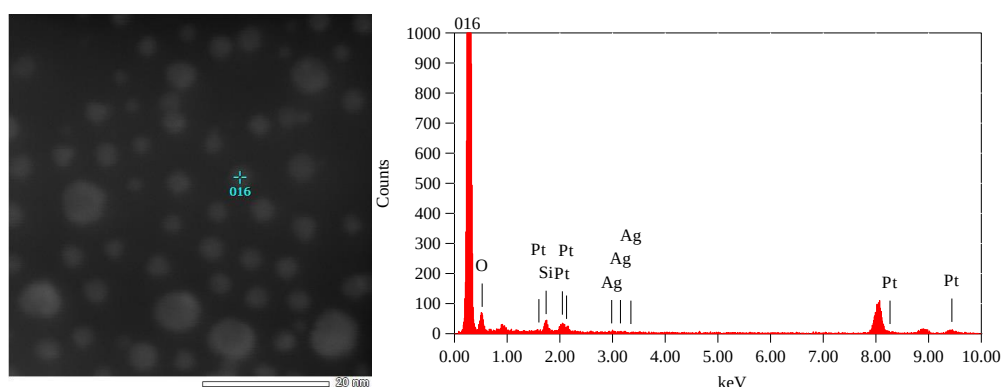


Figure 3.11 TEM and EDX results from near shell for C-Ag/Pt (25 mg PtCl₂)

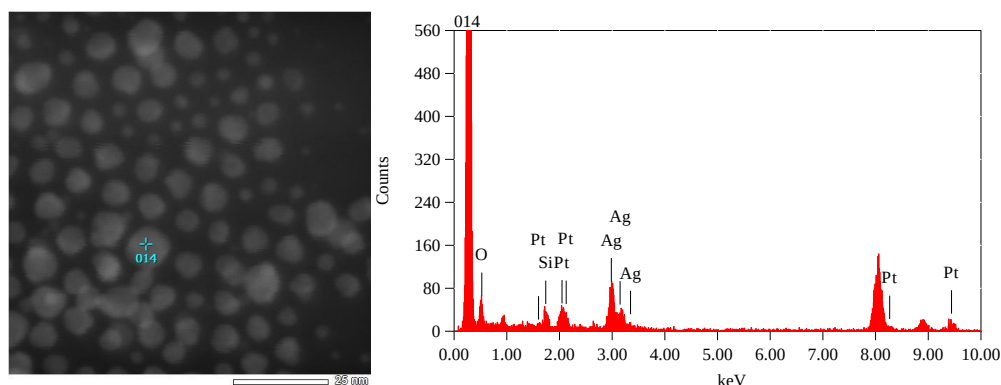


Figure 3.12 TEM images and EDX measurement from the core for C-Ag/Pt (25 mg PtCl₂)

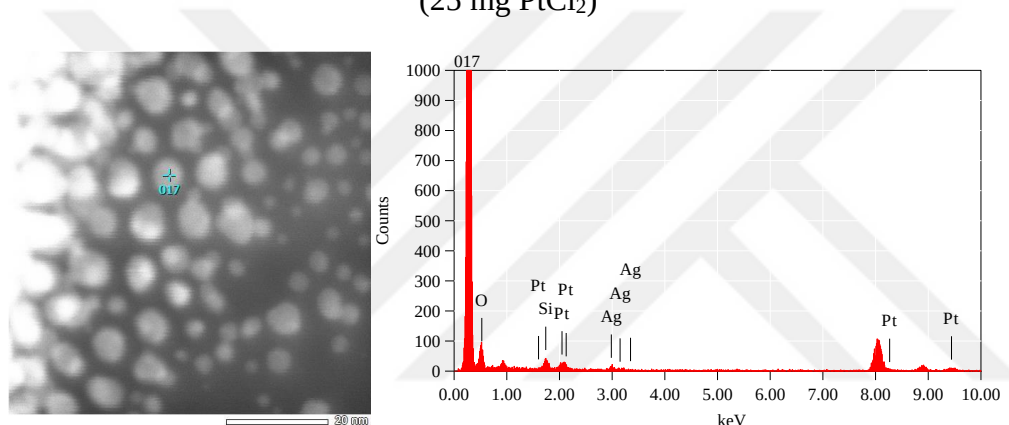


Figure 3.13 TEM images and EDX measurement from the near the shell for C-Ag/Pt (25 mg PtCl₂)

Figure 3.11, 3.12 and 3.13 are shown the TEM and related EDX measurement from the shell, core and near shell for C-Ag/Pt (25 mg PtCl₂) core-shell NPs. The peak near 3 keV represents the energy level of Ag L α while the energy level of Pt around 2 keV refers to Pt M α . The scale bar in the image of related figure is 20 nm. According to the EDX analysis, the compositions are 8.8% Ag and 91.2% Pt for the shell and 73.0% Ag and 27.0% Pt for the core, respectively. The results show the core-shell formation in the structure with Pt-rich shell and Ag-rich core. However, in Figure 3.13, the composition in focused near shell area is 41.3% Ag and 58.7% Pt. It may be due to

alloy formation. Consequently, C-Ag/Pt (25 mg PtCl_2) NPs contains both core-shell and alloy structures with heterogeneous particle dispersion.

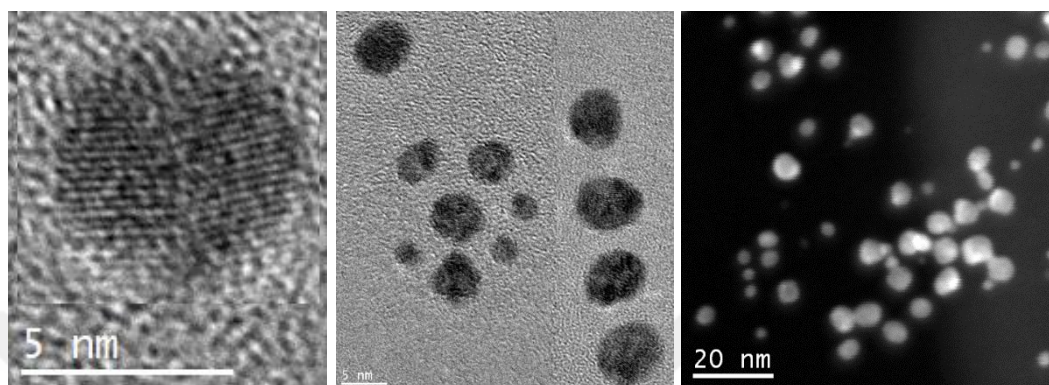


Figure 3.14 Particle distribution of C-Ag/Pt (35 mg PtCl_2) in TEM

Figure 3.14 demonstrates the particle distribution in TEM. According to this figure, it can be concluded that there is no monodispersed distribution in C-Ag/Pt (35 mg PtCl_2) in terms of particle size. The average particle size of NPs is ~ 6.5 nm.

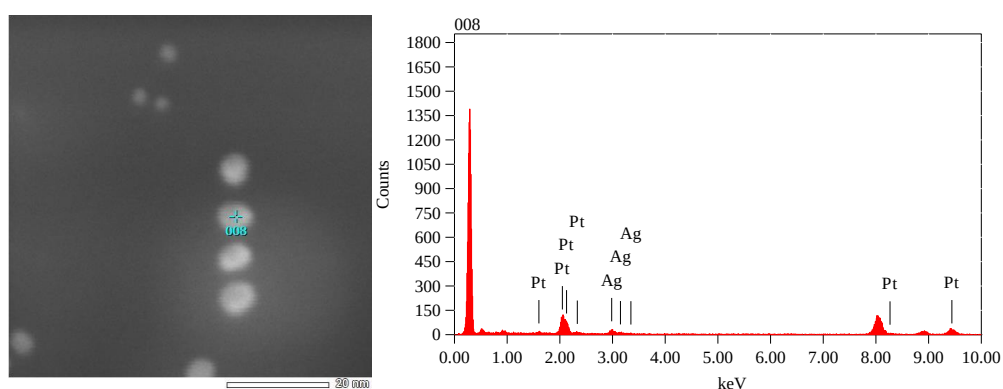


Figure 3.15 TEM images and EDX measurement from the shell for C-Ag/Pt (35 mg PtCl_2)

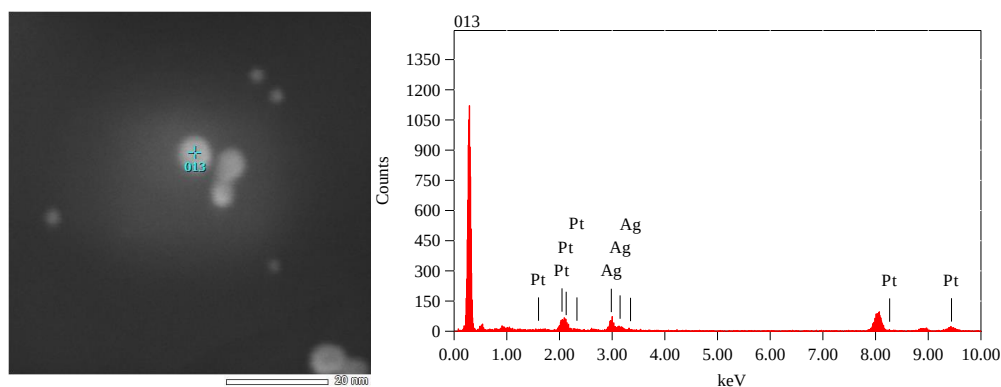


Figure 3.16 TEM images and EDX measurement from the core for C-Ag/Pt (35 mg PtCl₂)

Figure 3.15 and 3.16 demonstrate TEM images and related EDX measurement from the shell and the core for C-Ag/Pt (35 mg PtCl₂) core/shell NPs. Similar to the previous EDX figures, peaks at ~3 keV shows Ag L α while the ones at ~2 keV is for Pt M α . The compositions in Figure 3.15 are 17% Ag and 83% Pt while the sample contains 51% Ag and 49% Pt according to Figure 3.16. The results show the existence of Pt-rich shell and Ag-rich core in C-Ag/Pt (35 mg PtCl₂).

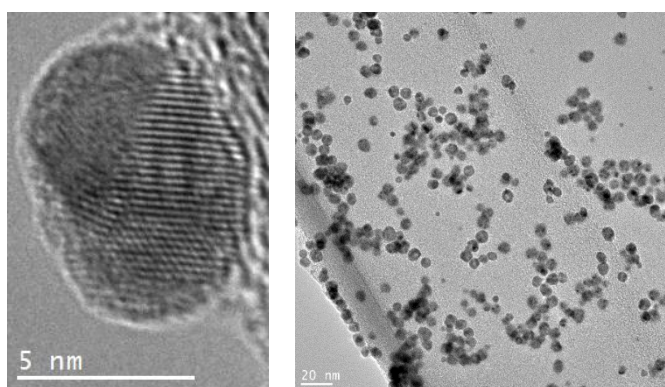


Figure 3.17 Particle distribution of C-Ag/Pt (45 mg PtCl₂) in TEM

Figure 3.17 shows the particle distribution of C-Ag/Pt (45 mg PtCl₂). The particle size distribution is better than the other two core-shell NPs. The average particle size of the NPs is ~8.5 nm.

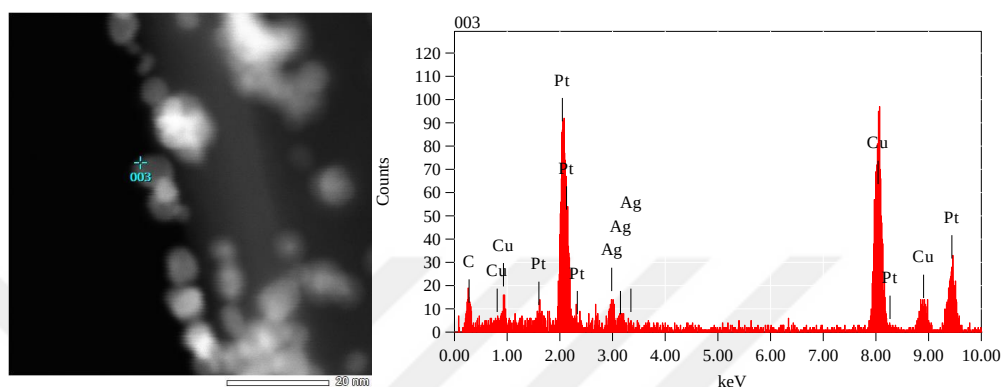


Figure 3.18 TEM images and EDX measurement from the shell for C-Ag/Pt (45 mg PtCl₂)

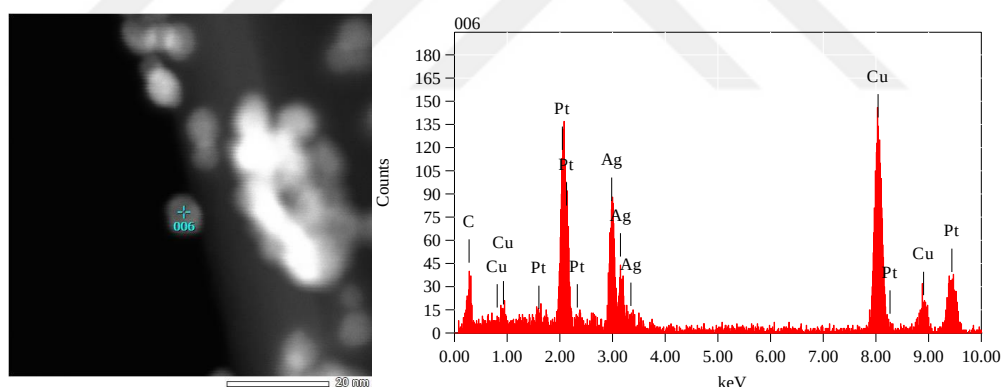


Figure 3.19 TEM images and EDX measurement from the core for C-Ag/Pt (45 mg PtCl₂)

Figure 3.18 and 3.19 show the amount of metals in EDX results. While the shell is Pt-rich based on Figure 3.18, the core has sufficient amount of Ag in Figure 3.19.

3.4 Electrochemical Activity Tests for C-Ag/Pt Nanoparticles

3.4.1 ECSA with C-Ag/Pt Nanoparticles containing different Pt amount

Figure 3.20 shows i_{peak} (mA) vs square root of scan rate for ECSA analysis (see Appendix III for details). The higher slope means higher ECSA based on equation (19). Vulcan XC72R presents the high surface area as indicated in Figure 3.20 which legitimates the reason of supporting at the first place. When carbon contains metals, the active area obviously shifts through the metal surfaces. Therefore, the indicated electrochemical active surface area for core-shell NPs originates from the metal surfaces. While commercial C-Pt gives the highest ECSA, the sample that has poor active area is C-Ag/Pt (25 mg PtCl_2) based on the slopes in Figure 3.20. The reason is due to problems with the particle distribution as indicated in TEM section above. Since C-Ag/Pt (45 mg PtCl_2) contains more Pt, its active surface area is higher compared to C-Ag/Pt (25 mg PtCl_2). However, both core-shell NPs have insufficient electrochemical active surface area even compared to carbon black. It is due to oxide formation and insufficient particle distribution, even agglomeration in some regions, as indicated in XPS results and TEM section.

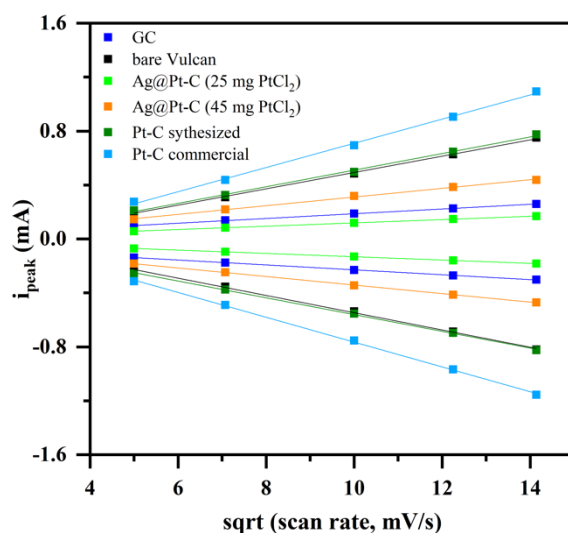


Figure 3.20 Peak current (mA) vs square root of scan rate (mV/s)

3.4.2 RDE for HER with C-Ag/Pt Core/Shell Nanoparticles containing different Pt amount

Figure 3.21 shows HER activities for C-Ag/Pt nanocatalysts with Cl based Pt precursor and Br based Pt salt in RDE. Pt amounts were adjusted to be same for C-Ag/Pt (25 mg PtCl_2) and C-Ag/Pt (33 mg PtBr_2) to compare their electrochemical activities in HER. In theory, since Pt and Br are metals whose structural properties are closer compared to Pt and Cl, the expectation was better harmony in the core-shell structure. However, from the Figure 3.21, PtCl_2 as a Pt precursor has better onset potential. Therefore, it was decided to continue with Cl based Pt precursor and entire project was set on this.

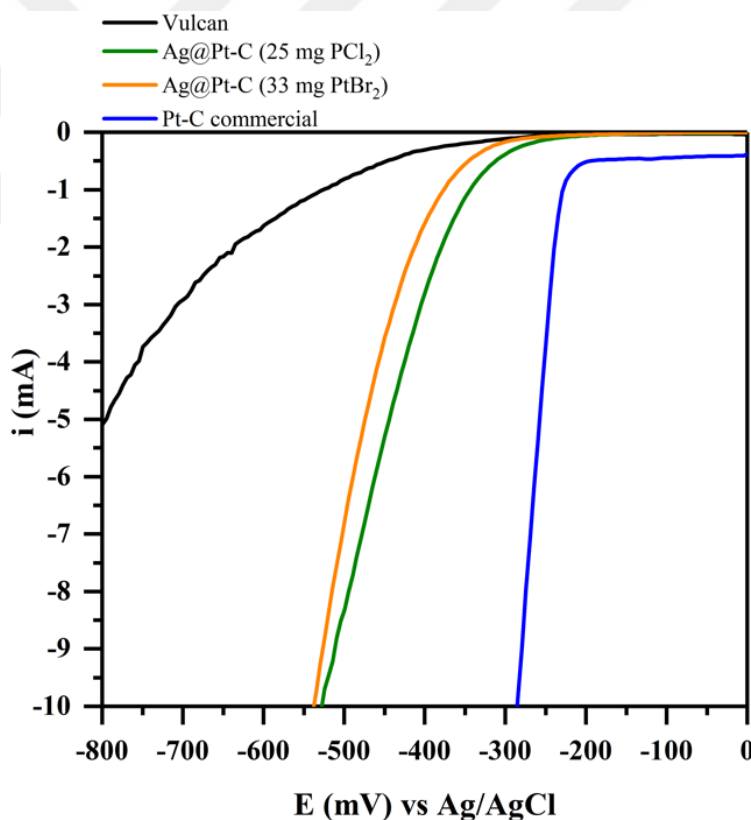


Figure 3.21 HER activities for C-Ag/Pt (25 mg PtCl_2) and (33 mg PtBr_2) core/shell NPs in RDE (0.5 M H_2SO_4 , 1600 rpm, 5 mV/s)

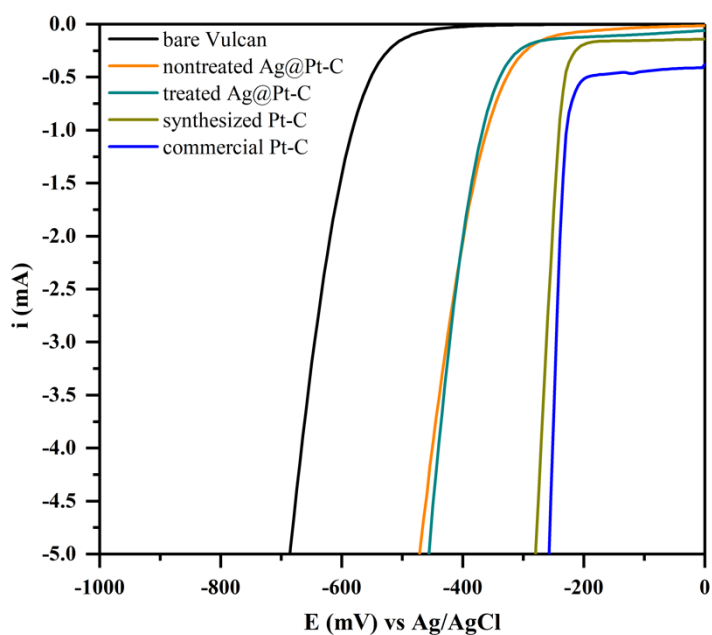


Figure 3.22 HER activities for nontreated and acetic acid treated C-Ag/Pt core/shell NPs in RDE (0.5 M H₂SO₄, 1600 rpm, 5 mV/s)

Figure 3.22 indicates the electrochemical activities of C-Ag/Pt core/shell NPs before and after chemical treatment with acetic acid for HER in RDE. In order to clean the structure from organics such as oleyl amine on the surface, NPs were washed with acetic acid. From Figure 3.22 above, it can be clearly seen that there is no significant contribution of acetic acid treatment on the enhancement of the activity for C-Ag/Pt core/shell NPs. The reason is that 0.5 M H₂SO₄ as an electrolyte already cleans the surface impurities during the activity tests. Hence, acetic acid treatment to remove organic compounds doesn't improve the electrochemical activity of core/shell NPs further. As a result, for the rest of the measurements, acetic acid treatment was not implemented to NPs.

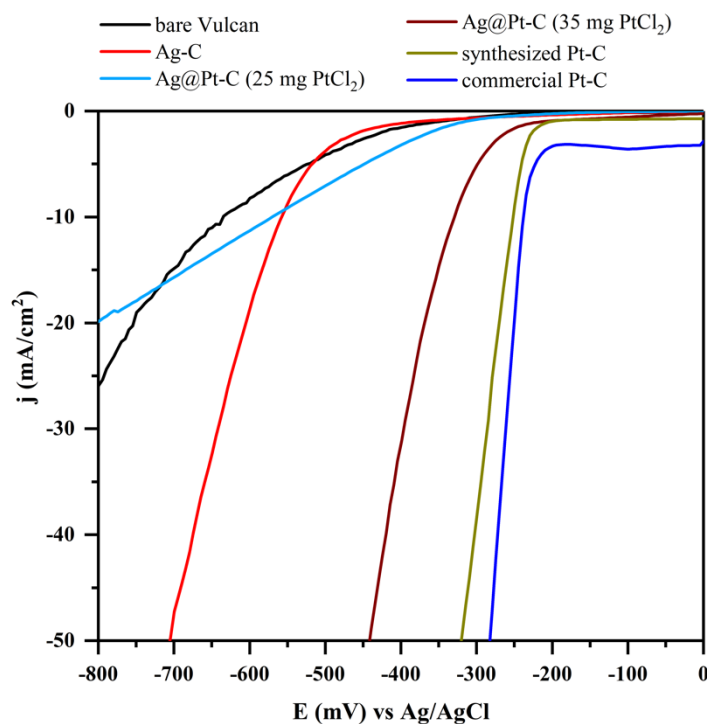


Figure 3.23 HER activity comparison for C-Ag/Pt (25, 35 and 45 mg PtCl₂) core/shell NPs in RDE (0.5 M H₂SO₄, 1600 rpm, 5 mV/s)

Table 3.3 Overpotential (mV) vs Ag/AgCl needed to reach -10 mA/cm² as a current density for HER in RDE based on Figure 3.23

Samples	Overpotential (mV) vs Ag/AgCl
bare Vulcan	-635
C-Ag	-554
C-Ag/Pt (25 mg PtCl ₂)	-570
C-Ag/Pt (35 mg PtCl ₂)	-329
synthesized C-Pt	-250
commercial C-Pt	-238

Figure 3.23 demonstrates the electrochemical activity measurements of C-Ag/Pt catalysts for HER in acidic media by using RDE while Table 3.3 exhibits the overpotential required to obtain -10 mA/cm^2 as the current density for the catalysts. The amount of catalysts dropped onto GC electrode are the same as $382 \text{ } \mu\text{g/cm}^2$ of catalysts for all samples. The general trend is that as Pt amount increases in the samples, the electrochemical activity in HER improves. However, it is a poor dependency between Pt content and the activity with no linear relation by taking ICP-MS results into account. In other words, it can be concluded that the incremental behavior in onset potentials with higher Pt amount is not only proportional with the amount of Pt but also strongly depending on the structure itself. For instance, according to Table 3.3, the overpotential required to obtain -10 mA/cm^2 for C-Ag/Pt (25 mg PtCl_2) is only 65 mV less than bare Vulcan. Also, although C-Ag/Pt (25 mg PtCl_2) has better onset potential compared to pure C-Ag NPs, the overpotential is 15 mV higher than C-Ag for -10 mA/cm^2 and it is getting worse in higher potential values. Those results point out the importance of surface structure in addition to the existence of Pt. According to ECSA results in Figure 3.20, the active surface area is dramatically insufficient for C-Ag/Pt (25 mg PtCl_2) even compared to bare Vulcan. Therefore, HER activity results are parallel with the poor active area. The reason of the inadequate activity is the blockage in Pt's active sides due to Ag effect. TEM-EDX results show the mixed behavior in this sample with both alloy and core-shell formation. TEM results also show that there is no monodispersity in these NPs. Therefore, the undesired particle distribution is also questioning the effect of the variation in thickness of the shell which can also be the reason of poor activity.

C-Ag/Pt (35 mg PtCl_2) NPs present a promising activity as core-shell NPs. The overpotential required for -10 mA/cm^2 is improved as 241 mV compared to C-Ag/Pt (25 mg PtCl_2). Also, it has better onset potential with higher current densities. The better activity result of these NPs compared to C-Ag/Pt (25 mg PtCl_2) even though they contain similar amount of Pt according to ICP-MS results in Table 3.1 are due to better structure and homogeneity in particle distribution. Also, based on Table 3.3, the

overpotential for C-Ag/Pt (35 mg PtCl₂) is 90 mV higher compared to commercial C-Pt. The result is quite promising when considering core-shell structure since it contains only half of Pt based on ICP-MS results. The difference come from the dispersity of the catalyst.

3.4.3 RDE for ORR with C-Ag/Pt Core/Shell Nanoparticles containing different Pt amount

Figure 3.24 demonstrates ORR activities of C-Ag/Pt catalysts in alkaline media with O₂ bubbling by using RDE, which is used to increase the solubility of O₂ into aqueous environment for a better mass transfer with convection [49]. The trend among core-shell NPs such that the one containing 45 mg PtCl₂ has better activity and the ones with 25 mg and 35 mg PtCl₂ have similar activities in terms of onset potential is as expected based on ICP-MS results. The Pt content in NPs is relevant with the ORR activity in alkaline media. As Pt amount increases, the ORR activity recovers. For instance, the Pt content of C-Ag/Pt (45 mg PtCl₂) is 18.4% while it is 18.8% for commercial C-Pt according to ICP-MS results in Table 3.1. The overpotential required to have -10 mA/cm² are the same as -44 mV for both while their onset potentials and current densities at certain potential are quite similar which is convenient by taking into consideration of effect of Pt amount. Similarly, according to Table 3.1, the Pt contents are quite close for C-Ag/Pt (25 mg PtCl₂) and (35 mg PtCl₂). Therefore, the overpotentials needed for -1 mA/cm² are almost same for these two samples, accordingly. According to XPS results, catalysts have oxides on their surface. The amount of oxides changes from sample to sample which also effects the current obtained at certain overpotential.

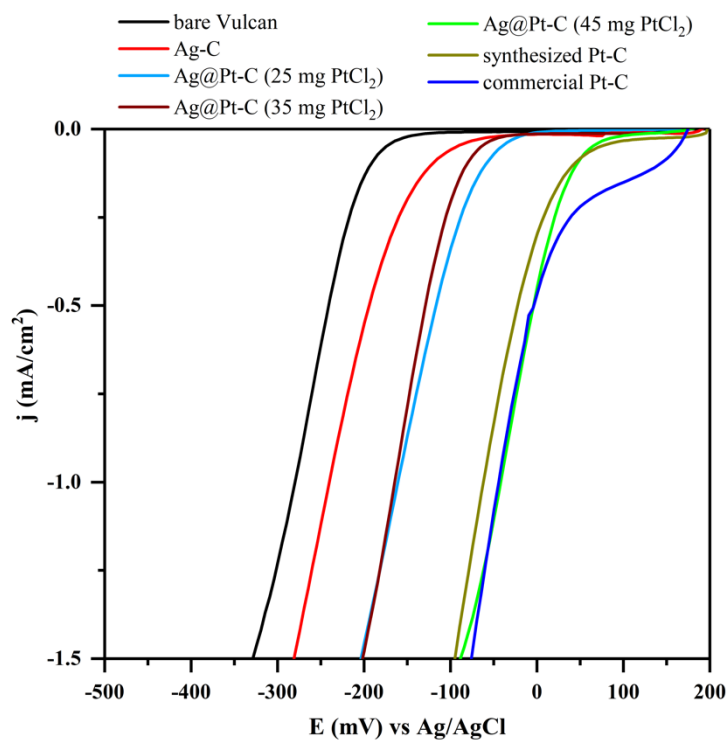


Figure 3.24 ORR activity comparison for C-Ag/Pt (25, 35 and 45 mg PtCl₂) core/shell NPs in RDE (O₂ purging, 0.1 M KOH, 1000 rpm, 5 mV/s)

Table 3.4 Overpotential (mV) needed to reach -1.0 mA/cm² as a current density for ORR in RDE based on Figure 3.24

Samples	Overpotential (mV) vs Ag/AgCl
bare Vulcan	-280
C-Ag	-240
C-Ag/Pt (25 m PtCl ₂)	-161
C-Ag/Pt (35 m PtCl ₂)	-164
C-Ag/Pt (45 m PtCl ₂)	-44
synthesized C-Pt	-99
commercial C-Pt	-44

3.4.4 CV curves for ORR with C-Ag/Pt Core/Shell Nanoparticles containing different Pt amount

Figure 3.25 demonstrates CV curves of ORR for C-Ag/Pt catalysts in alkaline media. The potential below -550 mV represents the hydrogen region above shows the oxygen region. The cathodic sweep below -550 mV is where Pt-H bond forms and the potential above -900 mV is where hydrogen evolution takes place. On the other hand, anodic sweep in the same region demonstrates where Pt-H oxidation occurs. Between -550 to -450 mV, the current flow is due to electrical double layer. Above -450 mV in anodic side, chemisorption of oxide begins with

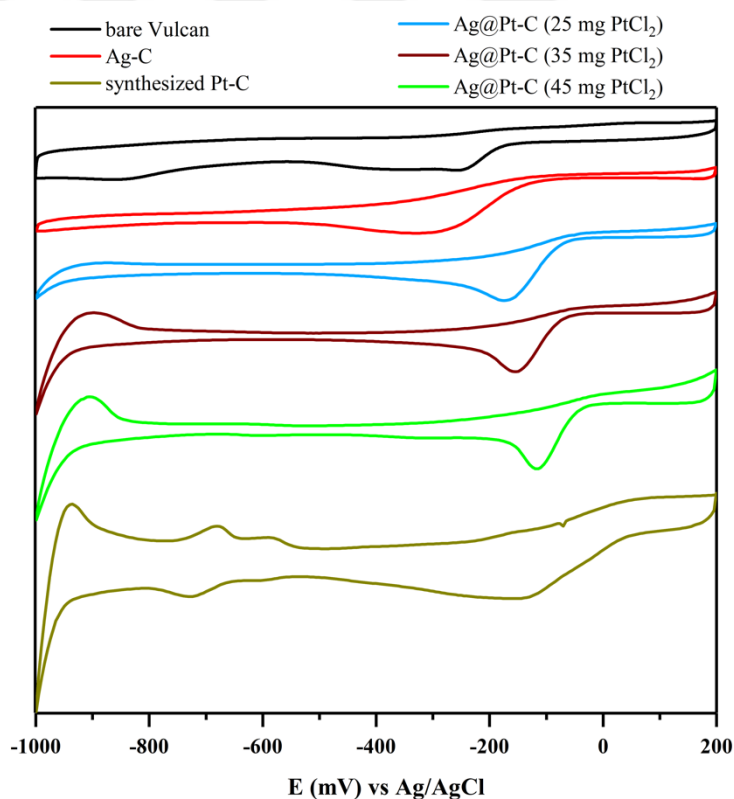
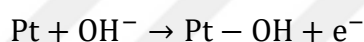
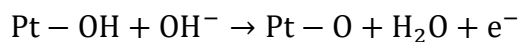


Figure 3.25 CV curves for ORR with C-Ag/Pt (25, 35 and 45 mg PtCl₂)
(O₂ purging, 0.1 M KOH, 5mV/s)

While above -200 mV,



takes place. In the cathodic side, on the other hand, Pt-O reduction begins. In other words, potentials between -200 to 200 mV in cathodic sweep is where ORR occurs. In the light of these information, the anodic peak above -850 mV is the certain proof of Pt existence. For instance, while C-Pt and all C-Ag/Pt have the related peak, C-Ag and bare Vulcan have no peak at specified potential. Also, the peak broadening gives further idea about Pt. The broader peak means the higher amount of coordinated Pt on the surface. Peaks become narrower as initial Pt amount added increases from C-Ag/Pt (25 mg PtCl₂) to C-Pt. Therefore, the orderly aligned Pt shell becomes appear with the increment in Pt content.

Meanwhile, the cathodic side in the same range (above -850 mV) is where hydrogen evolution takes place. The sudden decline represents the onset potential of the reaction. Also, the steep line provides the information about the strong effect of Pt in the structure by showing the existence of Pt-H adsorption. Therefore, from the related peak, as Pt amount increases, the line becomes appear and steep. For instance, there is no sign of hydrogen evolution peak for bare Vulcan and C-Ag which is rational since they contain no Pt.

In the oxygen region, from bottom curve to top, as Pt content decreases the onset potentials become closer to positive side which is consistent with ICP-MS results. The peak broadening from kinetic region to mass transport region in ORR is due to oxides in the structures particularly in C-Pt and C-Ag.

CHAPTER 4

SYNTHESIS AND CHARACTERIZATION OF MODIFIED PT NANOPARTICLES FOR ELECTROCHEMICAL APPLICATIONS

4.1 Literature Review

Synthesis method is the most challenging part affecting all parameters such as particle size, structure, shape and surface concentration. Therefore, proper method with proper precursors should be used for structurally precise NPs.

J. Gao et. al. focused on the controlling optical properties of the composite hollow structures by synthesizing bimetallic hollow AgPt by using AgNO_3 and H_2PtCl_6 as precursors in the existence of hydrazine as a reducing agent in galvanic replacement method. They observed a red shift in UV-Vis spectra with increasing Pt amount and showed that the surface plasmon resonance peak could be tuned for hollow bimetallic AgPt NPs [50].

M.R. Kim et. al. suggested the synthesis of hollow AgPt nanocomposites by using AgNO_3 and H_2PtCl_6 as precursors in the existence of PVP and ethylene glycol. They grew Pt shell on the hollow Ag structure via galvanic replacement method and removed the residual Ag by using chemical leaching with 0.5 M HNO_3 . They indicated that the increase in $[\text{Pt}]:[\text{Ag}]$ enhances the catalytic activity by accelerating the reaction rate of rhodamine B and KBH_4 reaction [51].

Hollow Pt nanostructures in electrochemical applications are promising with their superior performance. F. Shao et. al. suggested that AgPt hollow alloy nanostructures are active for hydrogen evolution reaction in alkaline media by using PVP as a

stabilizer and cytosine as a dispersing agent. The process increased the electrochemical surface area of the catalyst four times more compared to commercial Pt-C and thereby, contributed to enhanced HER activity by shifting the required overpotential to more positive values in acidic media [52].

T. Lian et al. studied porous hollow Pt NPs with coral-like shape by focusing on the importance of mesocrystal structures with basically higher porosity and crystalline defects for enhancing the electrochemical activity in methanol oxidation reaction. After they synthesized AgPt coral-like complex with Pt shell with AgNO_3 and H_2PtCl_6 as Ag and Pt sources, respectively, they used chemical leaching method via 2 M HNO_3 to remove Ag and obtain the hollow mesocrystals. They observed improved electrocatalytic activity in parallel with the increased ECSA from core-shell to hollow structure [53].

J.N. Zheng et. al. studied one-pot solvothermal synthesis for hollow Ag/Pt supported with graphene-oxide for ethylene glycol reduction reaction. They investigated the importance of molar ratio of Pt to Ag, temperature, amount of reducing agent and carbon support on the catalysts' structure which affects the activity. [54].

4.2 Synthesis of Modified Pt Nanoparticles

In order to obtain tailored Pt NPs by removing Ag in the core from C-Ag/Pt core/shell NPs, dealloying process was applied via two methods: electrochemical leaching and chemical etching. For electrochemical leaching, anodic sweep was used with LSV from 0 up to 1 V. For chemical etching, C-Ag/Pt (25 mg PtCl_2) core/shell NPs were treated overnight with saturated HCl by conducting partial reflux at 60 °C, at first. Then, after characterizations and electrochemical activity tests, it was changed with 1 M HNO_3 for all C-Ag/Pt samples.

4.3 Characterization for Modified Pt Nanoparticles obtained via electrochemical and chemical leaching

4.3.1 Surface Characterization done by XPS

4.3.1.1 *C-Ag/Pt (25 mg PtCl₂) – core/shell and modified Pt obtained via electrochemical leaching and chemical leaching with sat'd HCl and 1 M HNO₃*

In Figure 4.1, Pt 4f and Ag 3d XPS spectra are shown for modified C-Ag/Pt-C (25 mg PtCl₂) via electrochemical leaching and chemical leaching with saturated HCl and 1 M HNO₃, separately. Pt 4f graph shows that Pt amount in the surface of the catalysts increases after applying anodic bias to C-Ag/Pt (25 mg PtCl₂) core/shell NPs based on the peak intensities. Meanwhile, 4f_{5/2} peaks are at 74.6 eV while 4f_{7/2} peaks are at 71.2 eV for C-Ag/Pt before and after anodic sweep. It expresses that both structures contain metallic Pt [44]. However, peaks do not overlap exactly in higher binding energy side of 4f_{5/2} which means that there is an oxide formation at least for the one of these two samples. Therefore, by checking peak to peak ratio and the shoulders in higher binding energy side of 4f_{5/2}, it can be clearly indicated that modified C-Ag/Pt (25 mg PtCl₂) via electrochemical leaching has platinum oxide in its surface structure. Meanwhile, it is obvious that sat'd HCl is also etching Pt in the shell when considering the dramatic intensity decrease. Hence, using sat'd HCl is not a suitable method to remove core compound. On the other hand, chemical etching with 1 M HNO₃ results with three peaks in Pt 4f XPS spectra in Figure 4.1. The species contribute these triple peaks are adsorbed oxygen on Pt surface, PtO and PtO₂ which have peaks at 75.1, 76.6 and 77.5 eV for 4f_{5/2} and 71.8, 73.4 and 74.2 eV for 4f_{7/2}, respectively [45].

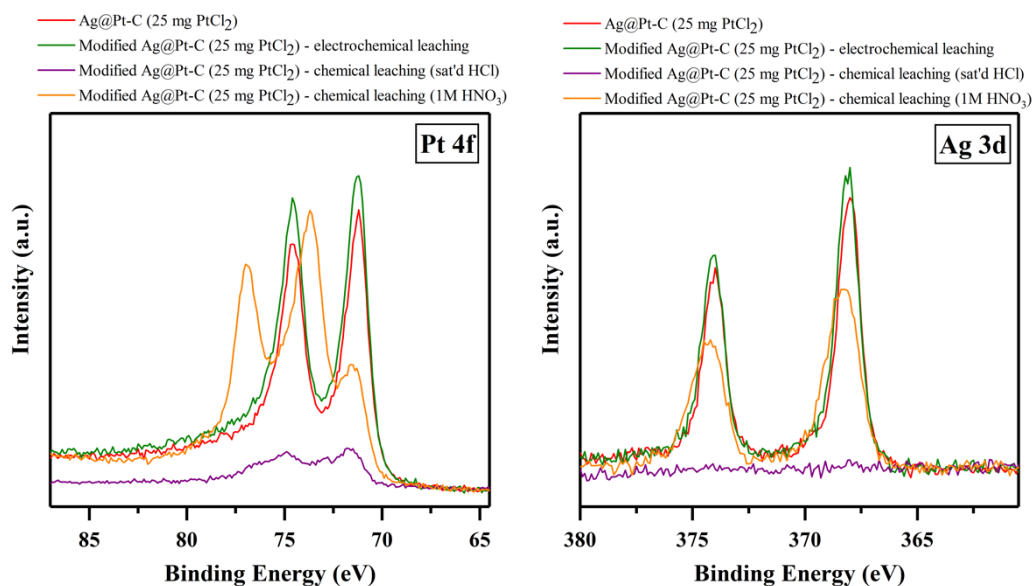


Figure 4.1 Pt 4f and Ag 3d XPS spectra from as prepared C-Ag/Pt (25 mg PtCl₂) and after electrochemical and chemical leaching with sat'd HCl and 1 M HNO₃

Ag 3d XPS spectra in Figure 4.1 shows that 3d_{3/2} and 3d_{5/2} peaks for C-Ag/Pt and modified C-Ag/Pt (25 mg PtCl₂) via electrochemical leaching are at 374 and 368 eV, respectively. These values are the indication of metallic Ag existence [55]. However, the Ag content in the surface does not decrease as expected with the anodic sweep although it converts Ag metals to Ag⁺ ions in the core due to Ag oxidation reaction. The reason is because the insufficiency of applied potential, i.e. less LSV than needed to remove all Ag from the core, causes surface segregation of Ag and thereby Ag is not leached totally from the core. In other words, Ag atoms mostly replace from the core to the shell as a result of anodic sweep.

Meanwhile, acid etching with sat'd HCl results in total removal of Ag from the sample since no peak observed in Ag 3d spectra for that sample. On the other hand, modified C-Ag/Pt (25 mg PtCl₂) by using 1 M HNO₃ for acid etching contains less Ag based on peak intensities. It means that chemical leaching via 1 M HNO₃ is an efficient method to remove the core by forming hollow structures as indicated in TEM images.

Normally, Ag behaves opposite manner when it bonds with oxygen. In other words, the oxide formation in metals shows themselves in higher binding energy sides while it is in lower energy side for Ag. Therefore, the peak at 369.2 eV for modified C-Ag/Pt via chemical leaching with 1 M HNO₃ cannot be attributed to oxide formation when metallic peaks are at 378.2 and 368.2 eV for 3d_{3/2} and 3d_{5/2}, respectively. The reason of the related shoulder is due to AgNO₃ formation [56].

In addition to C-Ag/Pt via acid etching with 1 M HNO₃, peak broadening and the peak shift for both core/shell and after electrochemically modified sample show the oxide formation in Ag₂O phase [57].

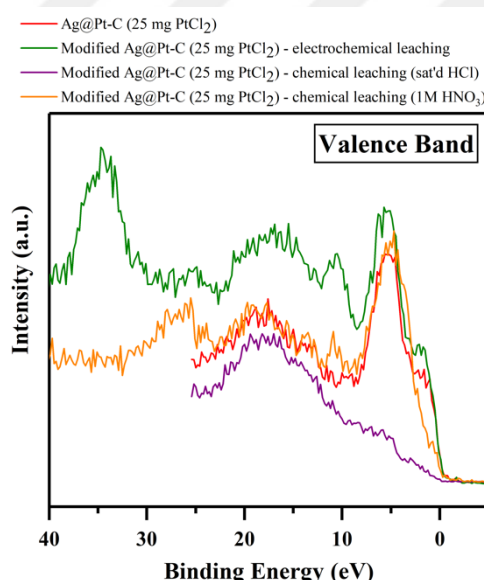


Figure 4.2 Valence Band XPS graph for C-Ag/Pt (25 mg PtCl₂) and its modified version after electrochemical and chemical leaching with sat'd HCl and 1M HNO₃

Valence band XPS spectra is shown in Figure 4.2 for modified C-Ag/Pt (25 mg PtCl₂). The peak at 5 eV for core-shell and modified samples via electrochemical leaching attribute to the presence of Pt mostly while the shoulder near Fermi level around 2 eV specifies the existence of Ag since Ag 4d peak is around 2 eV. On the other hand, there

is a slight peak at 5 eV and no peak observed at 2 eV in etched with HCl sample which indicates the partial removal and oxidation of Pt and complete etching of Ag.

4.3.1.2 *C-Ag/Pt (35 mg PtCl₂) – core/shell and modified Pt obtained via electrochemical leaching and chemical leaching with 1 M HNO₃*

Pt 4f and Ag 3d XPS spectra are shown in Figure 4.3 for C-Ag/Pt (35 mg PtCl₂) after modification by applying anodic bias and acid etching with 1M HNO₃, separately.

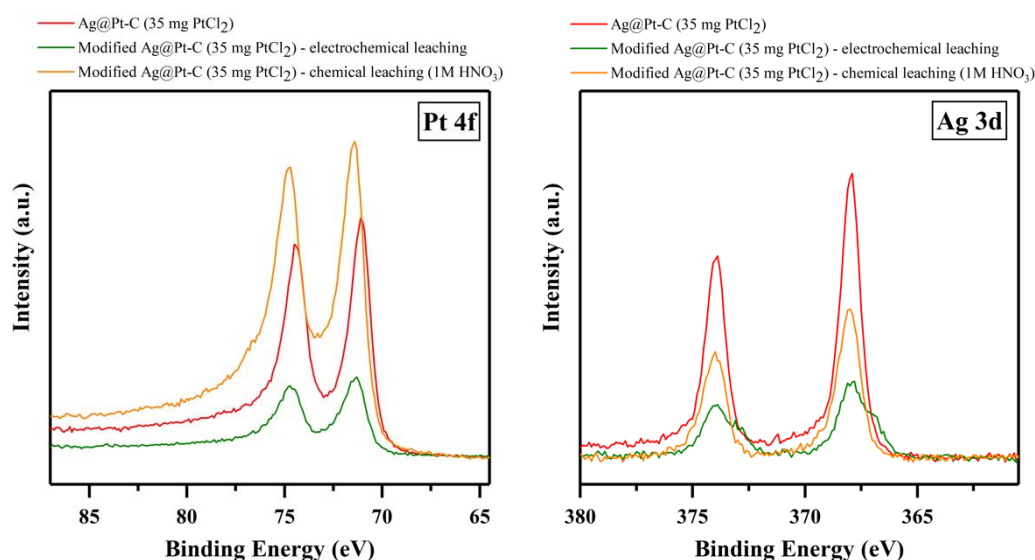


Figure 4.3 Pt 4f and Ag 3d XPS graphs for C-Ag/Pt (35 mg PtCl₂) and its modified version after electrochemical and chemical leaching with 1M HNO₃

Pt 4f spectra demonstrates the existence of metallic Pt for all samples. Also, the shoulder at 76.6 eV in higher energy side of 4f_{5/2} is due to PtO in the modified sample via acid etching [45].

The Ag 3d spectra in Figure 4.3 clearly show that applying anodic potential to remove Ag from the core is useful if enough number of anodic sweeps would be applied. However, more LSV means more structure distraction. The shoulder in the low binding energy side indicates the oxide formation on Ag in the form of Ag₂O during anodic cycling. Based on XPS results, it is quite convenient to use acid etching with 1 M HNO₃ for Ag removal from the core.

4.3.2 Microscopic Characterization with Imaging and Quantitative Analysis by using TEM and EDX for modified Pt nanoparticles including electrochemical and chemical leaching

Since the leaching process to remove Ag in the core was performed after the carbon support procedure, it was not easy to obtain high quality images from TEM due to carbon signals.

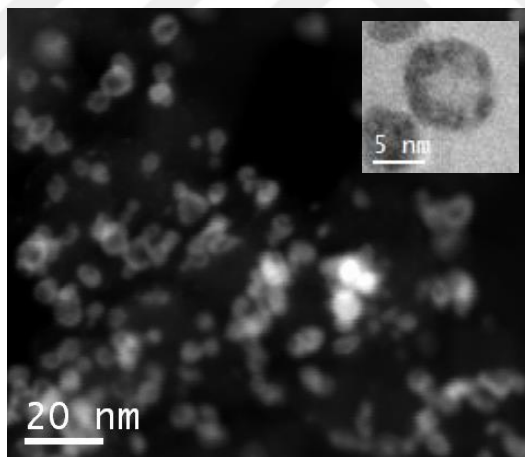


Figure 4.4 Modified C-Ag/Pt (25 mg PtCl₂) via chemical treatment with 1M HNO₃

Figure 4.4 indicates the modified C-Ag/Pt (25 mg PtCl₂) after HNO₃ etching. As it can be clearly seen from the figure, particularly from the one with 5 nm as a scale bar, chemical leaching forms hollow structures. However, there are agglomerations in some part of the distribution. The average particle size of NPs, i.e. hollow structures,

did not change after acid treatment. Also, the thickness of the shell in hollow NPs is ~ 2 nm.

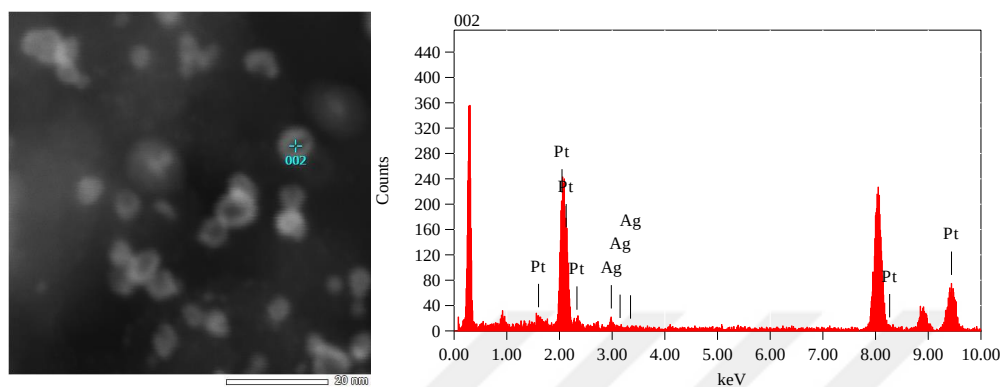


Figure 4.5 TEM images and EDX measurement from the shell for modified C-Ag/Pt (25 mg PtCl_2) via chemical leaching

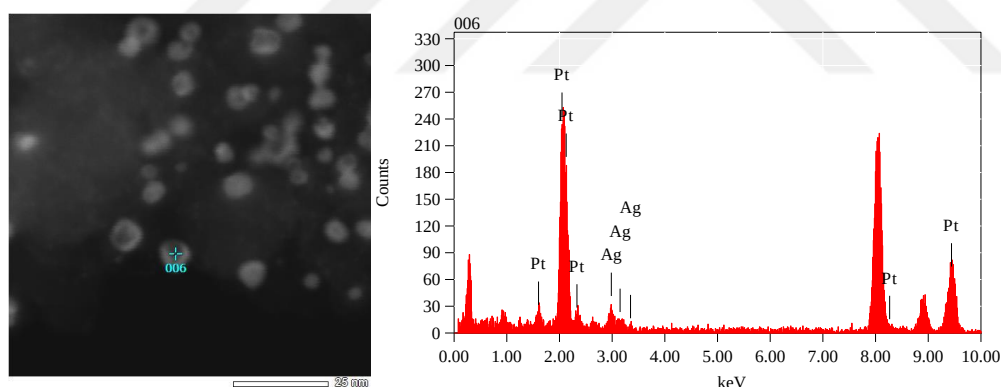


Figure 4.6 TEM images and EDX measurement from the core for C-Ag/Pt (25 mg PtCl_2) via chemical leaching with 1 M HNO_3

Figure 4.5 and 4.6 demonstrate the EDX results of given TEM images for modified C-Ag/Pt (25 mg PtCl_2) NPs via chemical leaching. According to EDX results, hollow NPs contain 4.2 wt% Ag and 95.8 wt% Pt in the shell while the percentage of Ag and Pt are 6.1 wt% and 93.9 wt%, respectively. Therefore, the formed structure has Pt-rich

shell and Ag etched core. This result indicates the successive etching of Ag from the core.

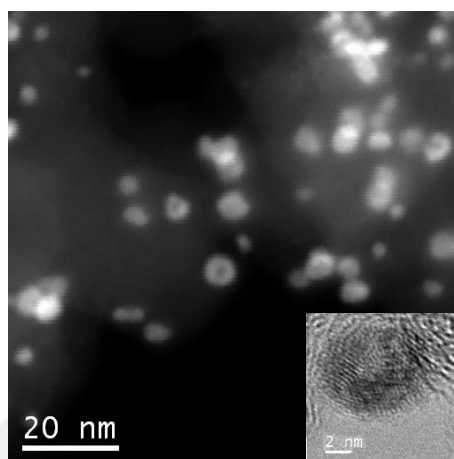


Figure 4.7 Modified C-Ag/Pt (35 mg PtCl_2) via chemical leaching

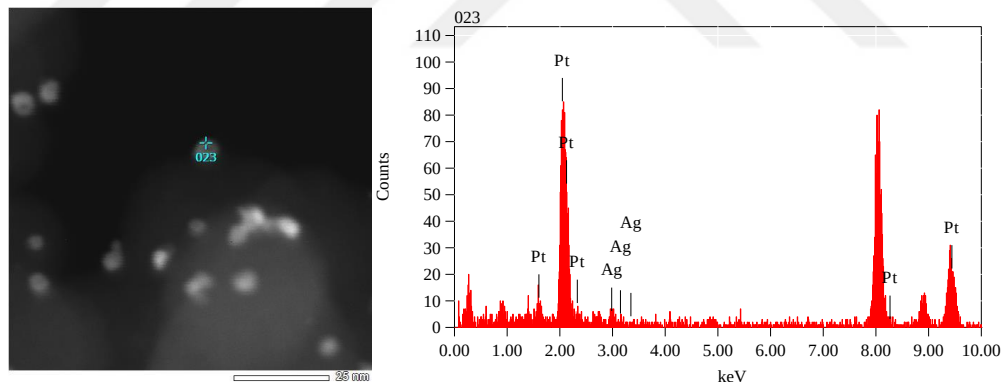


Figure 4.8 TEM images and EDX measurement from the shell for C-Ag/Pt (35 mg PtCl_2) via chemical leaching

Figure 4.7 demonstrates modified C-Ag/Pt (35 mg PtCl_2) via acid etching with 1 M HNO_3 . The hollow structures are seen in dark field TEM. Also, compositions are 4.9 wt% of Ag and 95.1 wt% of Pt near core EDX graph in Figure 4.8. The shell thickness was calculated as ~ 2.1 nm.

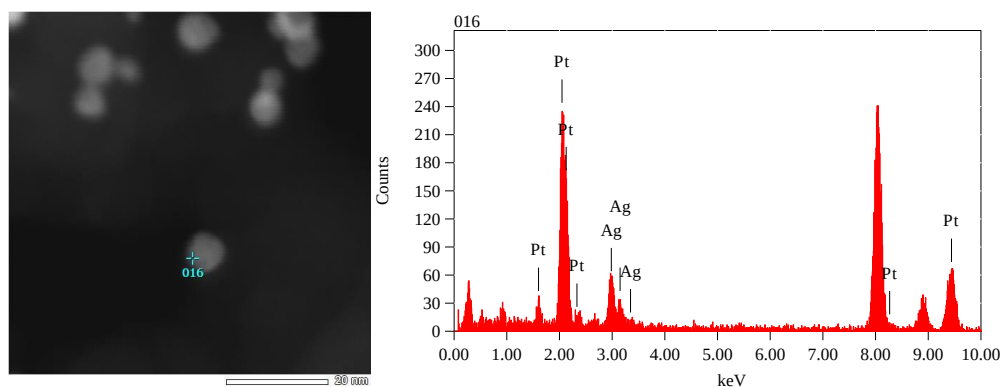


Figure 4.9 TEM images and EDX measurement from the shell for C-Ag/Pt (45 mg PtCl_2) via electrochemical leaching

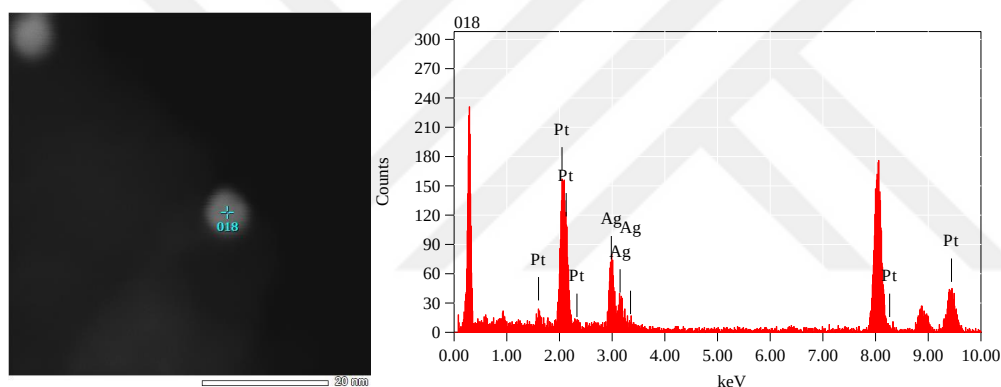


Figure 4.10 TEM images and EDX measurement from the core for C-Ag/Pt (45 mg PtCl_2) via electrochemical leaching

Figure 4.9 and 4.10 show the TEM images and their EDX results for C-Ag/Pt (45 mg PtCl_2) after anodic bias. Compositions at core are 33.3% Ag and 66.7% Pt while shell contains 19.6% Ag and 80.4% Pt. No hollow structure was observed based on the figures above.

4.4 Electrochemical Activity Tests for Modified Pt Nanoparticles obtained via electrochemical and chemical leaching

4.4.1 RDE for HER with modified Pt nanoparticles

Figure 4.11 demonstrates HER activities for modified C-Ag/Pt NPs via electrochemical leaching in RDE. The modification of C-Ag/Pt NPs by applying anodic potential to convert Ag^0 atoms to Ag^+ ions is a practical method to implement. The challenging point of the method is to make sure about the removal of approximately all Ag atoms from the structure by preventing the accumulation of Ag atoms on the surface and the aggregation. For instance, P. Strasser and coworkers performed 200 cycles of CV to remove Cu atoms from C-Cu/Pt core/shell NPs and they succeeded [58]. However, here, the number of LSV performed is five which causes the aggregation of NPs which blocks the surface activity as shown in TEM section. Therefore, these surface destructions cause poor HER activity for modified C-Ag/Pt (25 mg PtCl_2) applied anodic potential. As another reason of poor electrochemical activity is due to the existence of uncoordinated Pt atoms on the surface after modification as it will be discussed in CV for ORR section below. C-Ag/Pt (25 mg PtCl_2) has the lowest amount of Pt in the shell. Therefore, surface segregation of Ag after potential applied destructs Pt shell more than the other two samples. As a result, uncoordinated Pt atoms form on the shell. The acidic electrolyte affects these uncoordinated Pt atoms on the surface more and therefore, C-Ag/Pt (25 mg PtCl_2) NPs behaves more like C-Ag rather than showing any effect of Pt existence with those remaining on the surface unorderedly.

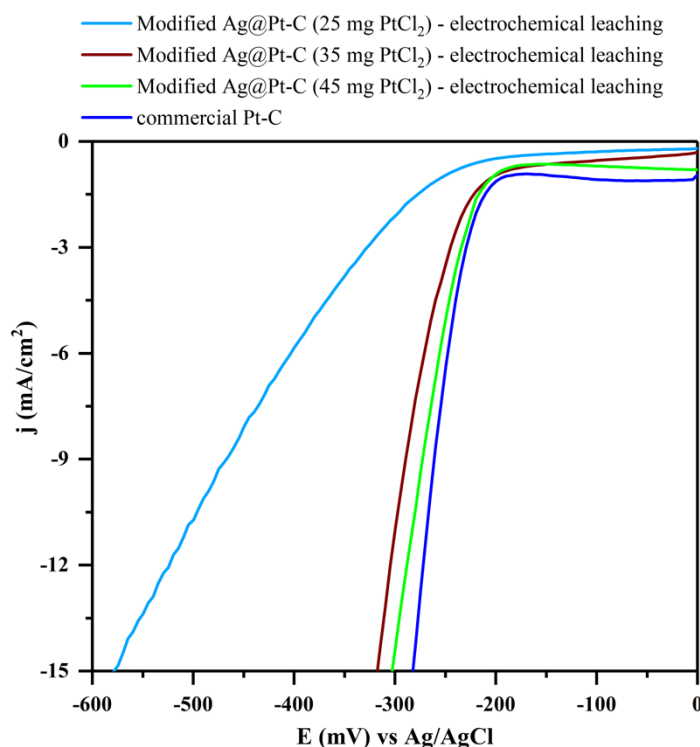


Figure 4.11 HER activity comparison for modified C-Ag/Pt (25, 35 and 45 mg PtCl_2) via electrochemical leaching in RDE (0.5 M H_2SO_4 , 1600 rpm, 5 mV/s)

On the other hand, the method works properly in other two samples by taking improved electrochemical activity into account. The slight difference in onset potentials and currents obtained between C-Ag/Pt (35 mg PtCl_2) and (45 mg PtCl_2) comes from the difference in number of Ag on the surface of the catalysts. According to XPS results, C-Ag/Pt (45 mg PtCl_2) contains more Ag. It means that even if the number of LSV applied is the same for two catalyst, the number of Ag removing from the core and segregating to the surface is different which directly affects the active sides of Pt. Moreover, the reason why the activity of modified NPs is close but not better than commercial C-Pt is due to these leftover Ag on the surface. Nevertheless, there is a huge improvement of electrochemical activity from core/shell to modified NPs based on overpotential required to obtain $-10 \text{ mA}/\text{cm}^2$. For instance, the enhancement compared to core/shell NPs is 83 mV, 35 mV and 90 mV, respectively,

for modified C-Ag/Pt (25, 35 and 45 mg PtCl_2). In addition to the segregation, since step edges and kinks are the active sides of Pt, supplying energy to the structure changes the thermodynamic of the surface which leads to rearrangement of these active sides as a result of surface defects [59]. In this case, applying potential to remove Ag from the core results in the dissolution of Ag^+ ions in the electrolyte. However, since enough LSV voltammetry was not performed, the partial dissolution occurs and the process results in the structural deformation and creates defects on the surface of catalyst with Pt shell. These defects increase the surface to volume ratio of Pt leading to enhanced electrocatalytic activity since HER is the reaction with fast kinetics. Also, the modification with anodic sweep recovers the slope of curves for both methods which means the increase of current obtained.

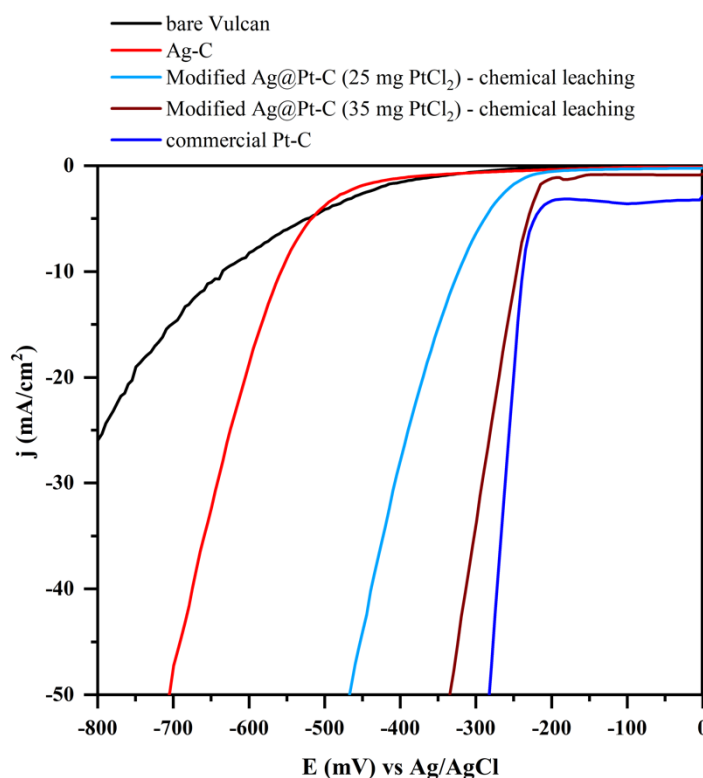


Figure 4.12 HER activity comparison for modified C-Ag/Pt (25 and 35 mg PtCl_2) via chemical leaching in RDE (0.5 M H_2SO_4 , 1600 rpm, 5 mV/s)

Figure 4.12 shows the activity comparison among chemically leached C-Ag/Pt nanocatalysts for HER in RDE. According to TEM results, the modification of NPs by using acid etching forms hollow structures as Ag in the core is removed. The results from Ag 3d XPS spectra in Figure 4.1 and 4.3 indicate the etching of Ag from the core via chemical leaching. TEM-EDX results are also consistent by showing the decrease in the composition of Ag in hollow structures. However, according to both characterization technique, the existence of remaining Ag is obviously shown. Therefore, these results lead to partial leaching after the acid treatment. The overpotentials needed to obtain -10 mA/cm^2 -322, -246 and -238 mV for hollow Pt from C-Ag/Pt (25 mg PtCl_2) and (35 mg PtCl_2) and commercial C-Pt, respectively. The reason why hollow Pt (35 mg PtCl_2) has better activity is the well-structured hollow NPs compared to (25 mg PtCl_2) NPs which affects the active area where the adsorption takes place. Also, the improvement in HER can be explained via the increase in surface/volume ratio as a result of hollow shape as expected. Although the onset potential for modified C-Ag/Pt (35 mg PtCl_2) via acid treatment with 1M HNO_3 is slightly better than the commercial C-Pt, the reason why overall activity of commercial C-Pt is better due to higher current density is because there is still significant amount of Ag existing in the structure according to TEM-EDX results which shows that not only Pt sites contribute the activity but also leftover Ag affects the activity by blocking the edge sides of Pt. Consequently, the modification via chemical leaching with 1 M HNO_3 is indeed more convenient than via applying anodic bias since it removes large amount of Ag in the core without breaking the structure of NPs and by increasing the surface to volume ratio, coherently. Even partial removal of Ag makes modified catalysts act like pure C-Pt.

4.4.2 RDE for ORR with modified Pt nanoparticles

Figure 4.13 shows the electrochemical activity results of ORR in RDE for modified C-Ag/Pt (25, 35 and 45 mg PtCl₂) via electrochemical leaching. Even though the idea of electrochemically removing the Ag from the core with the help of Ag oxidation reaction is quite straightforward, the control in the method is challenging. At this point, number of LSV applied, potential ranges, exposure time are parameters affecting the leaching. Therefore, different catalysts behave differently since the coordination of the atoms varies from sample to sample. As the potential applied in a certain range, Ag atoms move from the core to the surface. The surface segregation changes from sample to sample since the structures and the number of Ag are different. Also, as a result of etched Ag atoms, vacancies form on the surface. These defects increase the surface to volume ratio of the catalysts which directly affects the electrochemical activity. For instance, the uncertain relation after the modification can be shown from the comparison of C-Ag/Pt (35 mg PtCl₂) and C-Ag/Pt (25 mg PtCl₂). Overpotential required to obtain -10 mA/cm² is -218 mV for C-Ag/Pt while it is -125 mV for C-Ag/Pt. Based on this 93 mV difference between the two, it can be easily said that the former one has poorer activity in ORR compared to the latter one. It is because the Ag atoms covered the active sides of Pt are in different orientation for two samples as a result of surface segregation. Since the binding energy of adsorbed oxygen in first electron transfer, which is also the rate determining step of ORR, highly depends on the surface structure, the segregation effect due to leftover Ag is more than the activity in HER. Furthermore, the one that gives best activity among modified catalysts in ORR is C-Ag/Pt (45 mg PtCl₂) which is not a coincidence since it contains Pt most. The reason why it does not give the better activity than commercial C-Pt although they contain the same amount of Pt based on ICP-MS results comes from again the effect of leftover Ag on the surface such as in the other samples. Therefore, the catalyst behave mostly like Pt is due to the effect of Pt content while surface segregation is the reason of poor activity in C-Ag/Pt (45 mg PtCl₂). According to XPS results, Ag on the

surfaces have oxide formation in the form of Ag_2O which also effects the activity negatively.

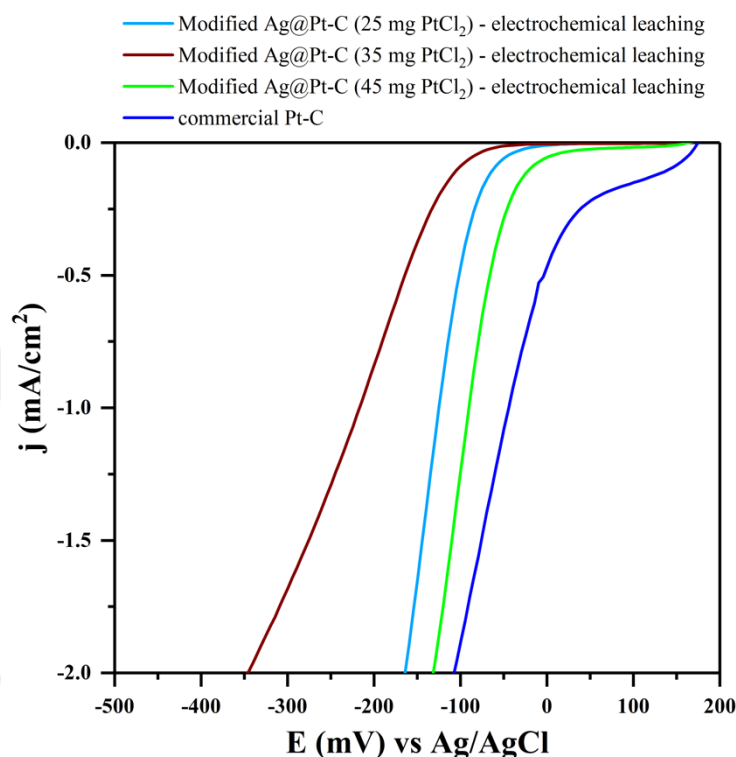


Figure 4.13 ORR activity comparison for modified C-Ag/Pt (25, 35 and 45 mg PtCl_2) via electrochemical leaching in RDE (O_2 bubbling, 0.1 M KOH, 1000 rpm, 5 mV/s)

Figure 4.14 shows ORR activities for modified C-Ag/Pt (25, 35 and 45 mg PtCl_2) obtained by etching with 1 M HNO_3 . The overpotentials required for -1 mA/cm^2 are -199 mV and -103 mV for modified C-Ag/Pt (25 mg PtCl_2) and (35 mg PtCl_2), respectively. According to Figure 4.14, the relation between Pt content and the activity preserves after modification via chemical leaching. According to XPS results, the structure contains Ag after the modification although both samples are in the hollow form. The different amount and coordination of Ag brings the difference in the amount of leftover Ag. Therefore, the improvement for two samples are different. For instance, modified C-Ag/Pt (25 mg PtCl_2) is close to C-Ag behavior while the effect of Pt is

dominant in C-Ag/Pt (35 mg PtCl₂). The defects also affect the enhancement in activity via vacancies. Also, increased surface to volume ratios due to hollow structures are another reason of improve electrochemical activity in ORR.

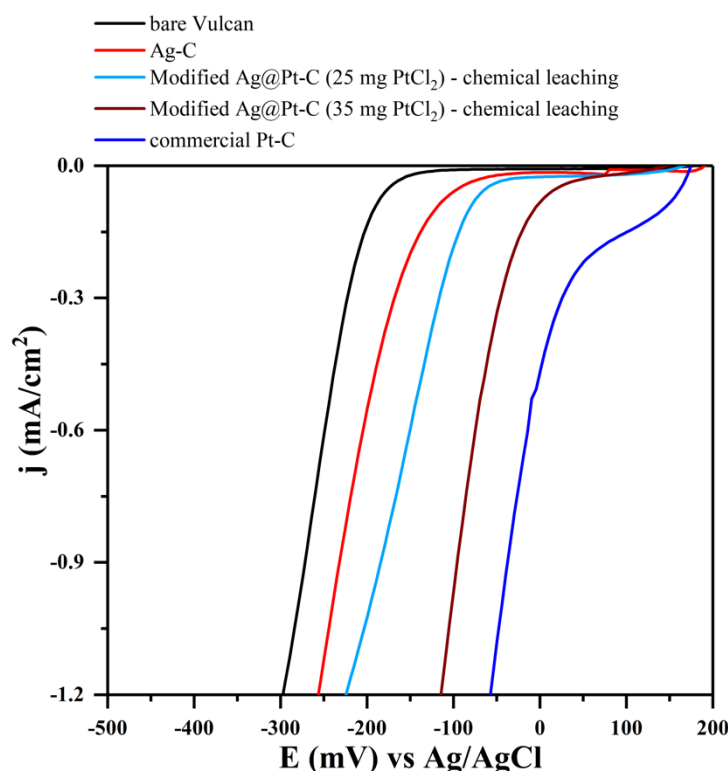


Figure 4.14 ORR activity comparison for modified C-Ag/Pt (25, 35 and 45 mg PtCl₂) via chemical leaching in RDE (O₂ bubbling, 0.1 M KOH, 1000 rpm, 5 mV/s)

4.4.3 CV curves for modified Pt nanoparticles

Figure 4.15 demonstrates the CV curves of ORR for modified NPs via anodic sweep in KOH solution with O₂ bubbling. The characteristic peaks in CV of ORR provide further understanding of the catalysts' structure. The peak at around -900 mV in the hydrogen region is where Pt-H bond forms in cathodic side and Pt-H oxidation occurs in anodic side. Therefore, the sharp peak in modified C-Ag/Pt (45 mg PtCl₂) exhibits the certain Pt presence after the modification. The peak intensity and broadening of the related peak indicate the ordered Pt on the surface with well-aligned shell structure.

Again, by taking the anodic hydrogen peak into account, the effect of Pt amount shows itself in modified C-Ag/Pt (45 mg PtCl_2) like before the modification since the Pt content is approximately same with commercial C-Pt in this sample. In the cathodic side of the same region, the onset potential of hydrogen evolution is the same with synthesized C-Pt with sudden decline, which means higher current density.

Although modified C-Ag/Pt (35 and 45 mg PtCl_2) and particularly synthesized C-Pt have apparently sharper peak in hydrogen region, it is not the case in modified C-Ag/Pt (25 mg PtCl_2) via anodic sweep. It indicates the structure of the shell of the NPs. For C-Ag/Pt (25 mg PtCl_2), the anodic peak around -900 mV is broader. It shows the existence of uncoordinated Pt atoms on the shell as a result of applied potential. Therefore, the surface segregation does not only cause the displacement of Ag from the core to the shell but also creates unordered alignment of Pt on the shell. Also, this unordered structure originates from the defects occurred as a result of leached Ag.

Also, straight line in the curves represents the presence of electrical double layer. Peaks in anodic side around -250 mV where oxide chemisorption begins with Pt-OH formation appears slightly for all samples. The main peaks concerned in Figure 4.15 is where oxygen reduction takes place.

The one with 45 mg PtCl_2 has the closest onset to the synthesized one. Modified NPs with 25 mg PtCl_2 follow it and the worse onset potential among them is 35 mg PtCl_2 . Even though the number of LSV applied is the same in all samples, since the structure of all are different and the amount of Ag in different sides are different because of inhomogeneity and particle size difference, the amount of Ag leached are not the same so the effect of electrochemical leaching on the activity is different in all samples. Therefore, the relation between Pt content and the activity is not preserved anymore after electrochemically modification. Also, the aggregation prevents the better electrochemical activity which is the case in anodic bias based on TEM images.

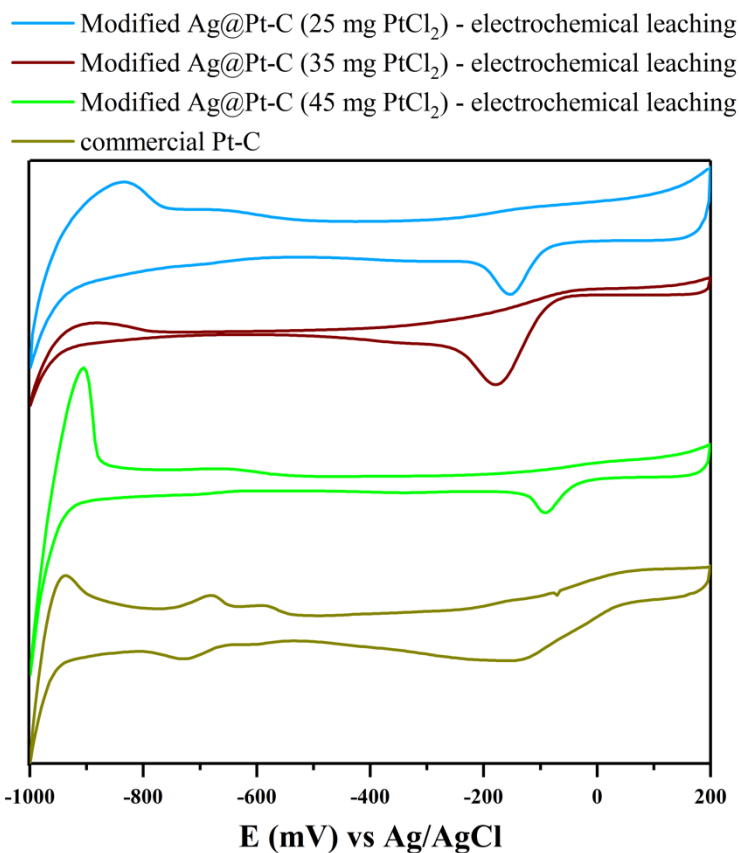


Figure 4.15 CV curves for ORR with modified C-Ag/Pt (25, 35 and 45 mg PtCl_2) via electrochemical leaching (O_2 bubbling, 0.1 M KOH, 5 mV/s)

Figure 4.16 demonstrates CV behaviors for modified C-Ag/Pt (25, 35 and 45 mg PtCl_2) obtained by acid treatment. The anodic peak intensity and shape in the hydrogen region clearly show the well aligned Pt on the surface for modified C-Ag/Pt (35 mg PtCl_2). The behavior of this modified catalyst is quite similar with synthesis C-Pt in the hydrogen region. Moreover, in the cathodic oxygen peak broadening indicate the oxide effect on C-Pt while the relatively sharp peak shows less amount of oxide presence in modified C-Ag/Pt (35 mg PtCl_2) which exhibits cleaner surface. The well-shape hollow structure shown in TEM section improves the activity as expected due to increased surface to volume ratio of the structure. Based on XPS and EDX results, there is still leftover Ag in the modified catalyst. Also, the remaining Ag atoms shows

themselves on the shell as well. Although, the electrochemical activity improvement is remarkable since the catalyst's behavior in CV is quite similar to C-Pt, the reason why the onset potential is not better than C-Pt is due to these leftover Ag in the structure.

On the other hand, even though chemically leached C-Ag/Pt (25 mg PtCl₂) has a certain hollow structure based on TEM images, the ORR activity is poor compared to C-Ag/Pt (35 mg PtCl₂). According to ECSA results, the active area of C-Ag/Pt (25 mg PtCl₂) core/shell NPs is inadequate for adsorption of the species on the surface and thereby, the active sites of Pt are not sufficiently used throughout the electrochemical reactions. Therefore, it is observed that chemical leaching does not resolve the blocked active sides for C-Ag/Pt (25 mg PtCl₂) even though it changes the structure of the NPs. On the contrary, the exposure to the acid makes the shell, which is the thinnest among other samples, uncoordinated. Therefore, C-Ag/Pt behaves closer to C-Ag instead of C-Pt.

The location of Ag atoms in the structure are different in both samples especially due to particle size differences. Therefore, the amount of Ag etched and remained in the structure are different. Thus, one of the main reasons of the difference in ORR onset potentials between C-Ag/Pt (25 and 35 mg PtCl₂) comes from varied particle size effect after modification. Also, the modified samples are not monodispersed based on dark field TEM images which affects the electrochemical activity too.

Consequently, acid etching to remove Ag core from the core/shell structure is quite convenient with improved activity observed; however, method with the acid concentration and exposure time used are not enough to remove all Ag from the catalyst which directly influences the electrochemical activity based on CV graph in Figure 4.16.

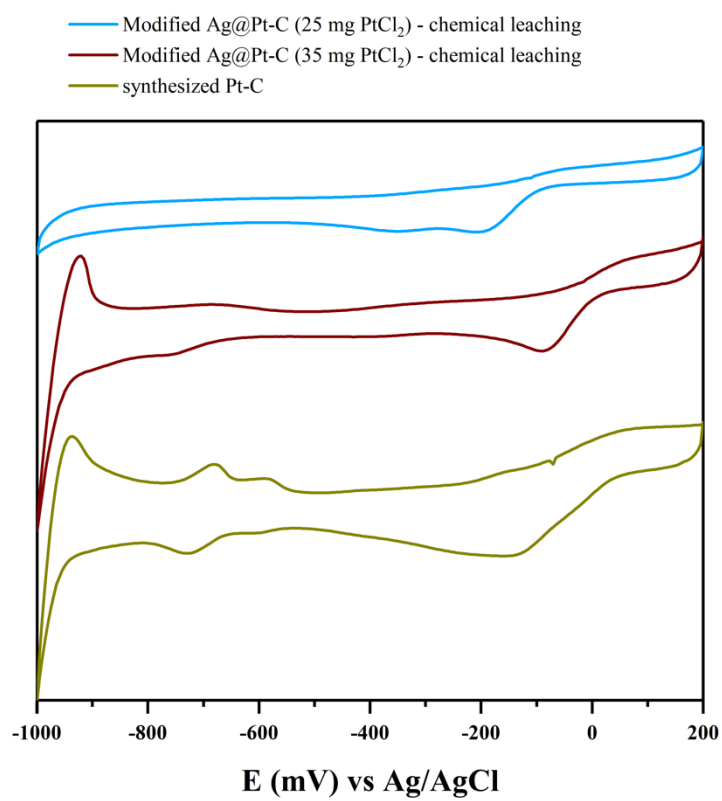


Figure 4.16 CV curves for ORR with modified C-Ag/Pt (25, 35 and 45 mg PtCl₂) via chemical leaching (O₂ bubbling, 0.1 M KOH, 5 mV/s)



CHAPTER 5

CONCLUSION

C-Ag/Pt core-shell and modified Pt NPs were investigated for HER and ORR. The aim was to enhance the electrochemical activities in both HER and ORR. For this purpose, C-Ag/Pt-C core-shell NPs were synthesized by using oleyl amine as strong surfactant with solvothermal colloidal method. The leaching of Ag in the core were performed by two different methods (i) by applying anodic bias to remove Ag and (ii) by acid etching in 1 M HNO₃. The Pt composition of C-Ag/Pt (25 mg PtCl₂) and (35 mg PtCl₂) contain approximately 45% less Pt while C-Ag/Pt (45 mg PtCl₂) behaves similar to the 20% commercial Pt-C. Also, the average particle sizes were determined as 7.4, 6.5 and 8.5 nm for 25, 35, and 45 mg PtCl₂, respectively. Hollow structures were obtained after acid etching to C-Ag/Pt NPs based on HRTEM and EDX results. According to XPS results, significant amount of oxide formation on the surface of the catalysts were observed after modifications with both methods which affected the electrochemical activity. The electrochemical activity tests show that the activity of synthesized core-shell NPs is poorly dependent on the amount of Pt containing. However, despite their contributions with various reasons, post modifications improve HER activity of all samples. For both C-Ag/Pt (25 mg PtCl₂) and C-Ag/Pt (35 mg PtCl₂), the samples exposed to acid treatment with 1 M HNO₃ give better onset potential than electrochemically modified samples. Moreover, the overpotential required to obtain -10 mA/cm² is almost same with commercial Pt-C for modified C-Ag/Pt (35 mg PtCl₂) via acid etching. The improvement in HER activity is due to defects on Pt surface in the catalysts which increase the surface to volume ratio as a result of the potential

applied. However, the situation was changed in ORR activities. While applying potential to NPs result in slightly better current density for C-Ag/Pt (25 mg PtCl₂), the activity becomes worse for C-Ag/Pt (35 mg PtCl₂) and (45 mg PtCl₂). The reason for worsening ORR activity after anodic sweep is due to surface segregation of Ag and agglomeration on the surface as a result of insufficient leaching. On the other hand, since the modifications via chemical leaching make them hollow, the surface to volume ratio increases; however, due to leftover Ag in the structure, the activity could not reach to the activity of commercial C-Pt. All in all, tuning the core-shell structures gives promising activity results in HER and ORR which are open to further investigations.

As future works,

1. C-Ag/Pt nanocatalyst will be optimized by varying the shell thickness of Pt for further understanding of the effect of thickness and strain effect.
2. Particle size of Ag in the core will be changed
3. Chemical etching with HNO₃ will be examined by changing the concentration and time to remove all Ag from the core.
4. Electrochemical leaching will be performed by increasing the number of cycles to remove all Ag from the core
5. C-Au/Pt NPs will be studied in a similar manner to investigate the strain effect.

REFERENCES

- [1] I. Dincer and C. Acar, "Review and evaluation of hydrogen production methods for better sustainability," *Int. J. Hydrog. Energy*, vol. 40, no. 34, pp. 11094–11111, Sep. 2015.
- [2] J. Wu *et al.*, "A review of PEM fuel cell durability: Degradation mechanisms and mitigation strategies," *J. Power Sources*, vol. 184, no. 1, pp. 104–119, Sep. 2008.
- [3] H. Wang and L. Gao, "Recent developments in electrochemical hydrogen evolution reaction," *Curr. Opin. Electrochem.*, vol. 7, pp. 7–14, Jan. 2018.
- [4] A. Lasia, "Hydrogen evolution reaction," in *Handbook of Fuel Cells*, American Cancer Society, 2010.
- [5] E. Navarro-Flores, Z. Chong, and S. Omanovic, "Characterization of Ni, NiMo, NiW and NiFe electroactive coatings as electrocatalysts for hydrogen evolution in an acidic medium," *J. Mol. Catal. Chem.*, vol. 226, no. 2, pp. 179–197, Feb. 2005.
- [6] L. Khotseng, "Oxygen Reduction Reaction," *Electrocatalysts Fuel Cells Hydrog. Evol. - Theory Des.*, Nov. 2018.
- [7] D. L. Fedlheim and C. A. Foss, *Metal Nanoparticles: Synthesis, Characterization, and Applications*. CRC Press, 2001.
- [8] "Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology | Chemical Reviews." [Online]. Available: <https://pubs.acs.org/doi/full/10.1021/cr030698%2B>. [Accessed: 13-Jul-2019].
- [9] J. N. Tiwari, R. N. Tiwari, and K. S. Kim, "Zero-dimensional, one-dimensional, two-dimensional and three-dimensional nanostructured materials for advanced electrochemical energy devices," *Prog. Mater. Sci.*, vol. 57, no. 4, pp. 724–803, May 2012.
- [10] "Novel development of nanoparticles to bimetallic nanoparticles and their composites: A review | Elsevier Enhanced Reader." [Online]. Available: <https://reader.elsevier.com/reader/sd/pii/S1018364717303518?token=18B4F9CA4992EE1CADBE6F030DCF3BBF875860F91E64F875BDB543CC4FD98C32E483A7F20DA84ECFFE7148D3C75FD130>. [Accessed: 13-Jul-2019].
- [11] F. D. Davalos, "Materials Science and Engineering - Callister (7 Ed.)."
- [12] M. B. Gawande *et al.*, "Core-shell nanoparticles: synthesis and applications in catalysis and electrocatalysis," *Chem. Soc. Rev.*, vol. 44, no. 21, pp. 7540–7590, 2015.
- [13] V. Mazumder, M. Chi, K. L. More, and S. Sun, "Core/Shell Pd/FePt Nanoparticles as an Active and Durable Catalyst for the Oxygen Reduction Reaction," *J. Am. Chem. Soc.*, vol. 132, no. 23, pp. 7848–7849, Jun. 2010.
- [14] "Fabrication and characterization of Fe@MoPO nanoparticles: Ion exchange behavior and photocatalytic activity against malachite green | Elsevier Enhanced Reader." [Online]. Available:

- <https://reader.elsevier.com/reader/sd/pii/S016773221630811X?token=85124EF0C4CFF02AE39B8872AE0AE7E8097F5264231C1138A35566B009B62DD2316530FC2932C4B7D1B0B3A9FC5E1B2A>. [Accessed: 13-Jul-2019].
- [15] P. Strasser *et al.*, “Lattice-strain control of the activity in dealloyed core–shell fuel cell catalysts,” *Nat. Chem.*, vol. 2, no. 6, pp. 454–460, Jun. 2010.
 - [16] J. Wu, P. Li, Yung-Tin (Frank) Pan, S. Warren, X. Yin, and H. Yang, “Surface lattice-engineered bimetallic nanoparticles and their catalytic properties,” *Chem. Soc. Rev.*, vol. 41, no. 24, pp. 8066–8074, 2012.
 - [17] H. You, Z. Peng, J. Wu, and H. Yang, “Lattice contracted AgPt nanoparticles,” *Chem. Commun.*, vol. 47, no. 47, pp. 12595–12597, 2011.
 - [18] “Tuning Nanoparticle Catalysis for the Oxygen Reduction Reaction - Guo - 2013 - Angewandte Chemie International Edition - Wiley Online Library.” [Online]. Available: <https://onlinelibrary.wiley.com/doi/full/10.1002/anie.201207186>. [Accessed: 13-Jul-2019].
 - [19] V. Stamenkovic *et al.*, “Changing the Activity of Electrocatalysts for Oxygen Reduction by Tuning the Surface Electronic Structure,” *Angew. Chem.*, vol. 118, no. 18, pp. 2963–2967, 2006.
 - [20] D. Wang *et al.*, “Structurally ordered intermetallic platinum–cobalt core–shell nanoparticles with enhanced activity and stability as oxygen reduction electrocatalysts,” *Nat. Mater.*, vol. 12, no. 1, pp. 81–87, Jan. 2013.
 - [21] B.-W. Zhang, H.-L. Yang, Y.-X. Wang, S.-X. Dou, and H.-K. Liu, “A Comprehensive Review on Controlling Surface Composition of Pt-Based Bimetallic Electrocatalysts,” *Adv. Energy Mater.*, vol. 8, no. 20, p. 1703597, Jul. 2018.
 - [22] N. Toshima and T. Yonezawa, “Bimetallic nanoparticles—novel materials for chemical and physical applications,” *New J. Chem.*, vol. 22, no. 11, pp. 1179–1201, Jan. 1998.
 - [23] M. Blosi *et al.*, “Bimetallic Nanoparticles as Efficient Catalysts: Facile and Green Microwave Synthesis,” *Materials*, vol. 9, no. 7, Jul. 2016.
 - [24] A. Eftekhari, “Electrocatalysts for hydrogen evolution reaction,” *Int. J. Hydrog. Energy*, vol. 42, no. 16, pp. 11053–11077, Apr. 2017.
 - [25] S. Koh and P. Strasser, “Electrocatalysis on Bimetallic Surfaces: Modifying Catalytic Reactivity for Oxygen Reduction by Voltammetric Surface Dealloying,” *J. Am. Chem. Soc.*, vol. 129, no. 42, pp. 12624–12625, Oct. 2007.
 - [26] A. J. Bard and L. R. Faulkner, *Electrochemical methods: fundamentals and applications*, 2nd ed. New York: Wiley, 2001.
 - [27] H.-H. Perkampus, *UV-VIS Spectroscopy and Its Applications*. Springer Science & Business Media, 2013.
 - [28] J. Zhu, “Surface Plasmon Resonance from Bimetallic Interface in Au–Ag Core–Shell Structure Nanowires,” *Nanoscale Res. Lett.*, vol. 4, no. 9, pp. 977–981, May 2009.
 - [29] R. Michalski, *Application of IC-MS and IC-ICP-MS in Environmental Research*. John Wiley & Sons, 2016.

- [30] P. Lucena, J. M. Vadillo, and J. J. Laserna, "Mapping of Platinum Group Metals in Automotive Exhaust Three-Way Catalysts Using Laser-Induced Breakdown Spectrometry," *Anal. Chem.*, vol. 71, no. 19, pp. 4385–4391, Oct. 1999.
- [31] P. van der Heide, *X-ray Photoelectron Spectroscopy: An introduction to Principles and Practices*. John Wiley & Sons, 2011.
- [32] S. Hüfner, *Photoelectron Spectroscopy: Principles and Applications*. Springer Science & Business Media, 2013.
- [33] R. Feng, M. Li, and J. Liu, "Synthesis of core-shell Au@Pt nanoparticles supported on Vulcan XC-72 carbon and their electrocatalytic activities for methanol oxidation," *Colloids Surf. Physicochem. Eng. Asp.*, vol. 406, pp. 6–12, Jul. 2012.
- [34] A. B. Soliman *et al.*, "Pt Immobilization within a Tailored Porous-Organic Polymer–Graphene Composite: Opportunities in the Hydrogen Evolving Reaction," *ACS Catal.*, vol. 7, no. 11, pp. 7847–7854, Nov. 2017.
- [35] A. I. H. Committee, *Engineered Materials Handbook, Desk Edition*. ASM International, 1995.
- [36] M. Liu, F. Chi, J. Liu, Y. Song, and F. Wang, "A novel strategy to synthesize bimetallic Pt–Ag particles with tunable nanostructures and their superior electrocatalytic activities toward the oxygen reduction reaction," *RSC Adv.*, vol. 6, no. 67, pp. 62327–62335, Jun. 2016.
- [37] A. Londono-Calderon, C. A. Campos-Roldan, R. G. González-Huerta, M. L. Hernandez-Pichardo, P. del Angel, and M. J. Yacaman, "Influence of the architecture of AuAgPt nanoparticles on the electrocatalytic activity for hydrogen evolution reaction," *Int. J. Hydrog. Energy*, vol. 42, no. 51, pp. 30208–30215, Dec. 2017.
- [38] C. Li and Y. Yamauchi, "Facile solution synthesis of Ag@Pt core-shell nanoparticles with dendritic Pt shells," *Phys. Chem. Chem. Phys.*, vol. 15, no. 10, pp. 3490–3496, 2013.
- [39] L. Chen, W. Zhao, Y. Jiao, X. He, J. Wang, and Y. Zhang, "Characterization of Ag/Pt core-shell nanoparticles by UV–vis absorption, resonance light-scattering techniques," *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.*, vol. 68, no. 3, pp. 484–490, Nov. 2007.
- [40] Z. Peng, J. Wu, and H. Yang, "Synthesis and Oxygen Reduction Electrocatalytic Property of Platinum Hollow and Platinum-on-Silver Nanoparticles," *Chem. Mater.*, vol. 22, no. 3, pp. 1098–1106, Feb. 2010.
- [41] V. K. LaMer and R. H. Dinegar, "Theory, Production and Mechanism of Formation of Monodispersed Hydrosols," *J. Am. Chem. Soc.*, vol. 72, no. 11, pp. 4847–4854, Nov. 1950.
- [42] V. K. L. Mer, "Nucleation in Phase Transitions.," vol. 44, no. 6, p. 8, 1952.
- [43] C. B. Murray, S. Sun, W. Gaschler, H. Doyle, T. A. Betley, and C. R. Kagan, "Colloidal synthesis of nanocrystals and nanocrystal superlattices," *IBM J. Res. Dev.*, vol. 45, no. 1, pp. 47–56, Jan. 2001.

- [44] J. F. MOULDER, "Handbook of X-Ray Photoelectron Spectroscopy," *Phys. Electron.*, pp. 230–232, 1995.
- [45] K. S. Kim, N. Winograd, and R. E. Davis, "Electron spectroscopy of platinum-oxygen surfaces and application to electrochemical studies," *J. Am. Chem. Soc.*, vol. 93, no. 23, pp. 6296–6297, Nov. 1971.
- [46] G. Michael. Bancroft, Ian. Adams, L. L. Coatsworth, C. David. Bennewitz, J. D. Brown, and W. D. Westwood, "ESCA study of sputtered platinum films," *Anal. Chem.*, vol. 47, no. 3, pp. 586–588, Mar. 1975.
- [47] B. Zhu *et al.*, "Preparation of carbon nanodots from single chain polymeric nanoparticles and theoretical investigation of the photoluminescence mechanism," *J. Mater. Chem. C*, vol. 1, no. 3, pp. 580–586, 2013.
- [48] S. Rather, M. Naik, S. W. Hwang, A. R. Kim, and K. S. Nahm, "Room temperature hydrogen uptake of carbon nanotubes promoted by silver metal catalyst," *J. Alloys Compd.*, vol. 475, no. 1, pp. L17–L21, May 2009.
- [49] X. Ge *et al.*, "Oxygen Reduction in Alkaline Media: From Mechanisms to Recent Advances of Catalysts," *ACS Catal.*, vol. 5, no. 8, pp. 4643–4667, Aug. 2015.
- [50] J. Gao, X. Ren, D. Chen, F. Tang, and J. Ren, "Bimetallic Ag–Pt hollow nanoparticles: Synthesis and tunable surface plasmon resonance," *Scr. Mater.*, vol. 57, no. 8, pp. 687–690, Oct. 2007.
- [51] M. R. Kim, D. K. Lee, and D.-J. Jang, "Facile fabrication of hollow Pt/Ag nanocomposites having enhanced catalytic properties," *Appl. Catal. B Environ.*, vol. 103, no. 1, pp. 253–260, Mar. 2011.
- [52] F.-Q. Shao, J.-J. Feng, Z.-Z. Yang, S.-S. Chen, J. Yuan, and A.-J. Wang, "Cytosine assisted aqueous synthesis of AgPt hollow alloyed nanostructures as highly active electrocatalyst for ethylene glycol oxidation and hydrogen evolution," *Int. J. Hydrog. Energy*, vol. 42, no. 39, pp. 24767–24775, Sep. 2017.
- [53] T. Li, H. You, M. Xu, X. Song, and J. Fang, "Electrocatalytic Properties of Hollow Coral-like Platinum Mesocrystals," *ACS Appl. Mater. Interfaces*, vol. 4, no. 12, pp. 6942–6948, Dec. 2012.
- [54] J.-N. Zheng, J.-J. Lv, S.-S. Li, M.-W. Xue, A.-J. Wang, and J.-J. Feng, "One-pot synthesis of reduced graphene oxide supported hollow Ag@Pt core-shell nanospheres with enhanced electrocatalytic activity for ethylene glycol oxidation," *J. Mater. Chem. A*, vol. 2, no. 10, pp. 3445–3451, 2014.
- [55] Y. Liu, R. G. Jordan, and S. L. Qiu, "Electronic structures of ordered Ag-Mg alloys," *Phys. Rev. B*, vol. 49, no. 7, pp. 4478–4484, Feb. 1994.
- [56] V. K. Kaushik, "XPS core level spectra and Auger parameters for some silver compounds," *J. Electron Spectrosc. Relat. Phenom.*, vol. 56, no. 3, pp. 273–277, Jun. 1991.
- [57] L. J. Gerenser, "Photoemission investigation of silver/poly(ethylene terephthalate) interfacial chemistry: The effect of oxygen-plasma treatment," *J. Vac. Sci. Technol. A*, vol. 8, no. 5, pp. 3682–3691, Sep. 1990.

- [58] P. Mani, R. Srivastava, and P. Strasser, “Dealloyed Pt–Cu Core–Shell Nanoparticle Electrocatalysts for Use in PEM Fuel Cell Cathodes,” *J. Phys. Chem. C*, vol. 112, no. 7, pp. 2770–2778, Feb. 2008.
- [59] Q.-S. Chen, F. J. Vidal-Iglesias, J. Solla-Gullón, S.-G. Sun, and J. M. Feliu, “Role of surface defect sites: from Pt model surfaces to shape-controlled nanoparticles,” *Chem. Sci.*, vol. 3, no. 1, pp. 136–147, Nov. 2011.





APPENDICES

Appendix I – ICP-MS Calculations

Table A.1 Raw data obtained in ICP-MS

Samples	Pt (ppm)	Ag (ppm)	m ₁ (mg)	m ₂ (mg)
commercial C-Pt	84.71	-	3.6	-
C-Ag	-	1.696	-	3.0
C-Ag/Pt (25 mg PtCl ₂)	48.90	1.682	4.1	4.3
C-Ag/Pt (35 mg PtCl ₂)	59.07	1.753	4.5	4.8
C-Ag/Pt (45 mg PtCl ₂)	94.38	1.518	4.1	4.1

In the Table A.1, m₁ and m₂ represent the total amount of catalyst weighed for Pt and Ag determination, respectively, for ICP-MS measurement. The prepared volume is 8 mL for all samples.

Sample Calculation for weight% determination

The sample calculation was made for wt% of Pt and Ag in C-Ag/Pt (25 mg PtCl₂). For wt% of Ag, 10 times dilution was implemented. Therefore, the dilution amount should be included in calculations.

$$\text{wt\% of Pt} = (48.90 \text{ ppm}) \times \left(\frac{10^{-3} \text{ mg/mL}}{1 \text{ ppm}} \right) \times (8 \text{ mL}) \times \left(\frac{1}{4.1 \text{ mg}} \right) \times 100 = 9.5\%$$

$$\begin{aligned} \text{wt\% of Ag} &= (1.753 \text{ ppm}) \times \left(\frac{10^{-3} \text{ mg/mL}}{1 \text{ ppm}} \right) \times (8 \text{ mL}) \times \left(\frac{1}{4.5 \text{ mg}} \right) \times (10) \times 100 \\ &= 3.1\% \end{aligned}$$

The same calculation was applied to all samples and Table 7.1 was obtained.

Appendix II – Baselines for Pt4f XPS Spectra

The baselines were drawn by using OriginPro 2017 64-bit.

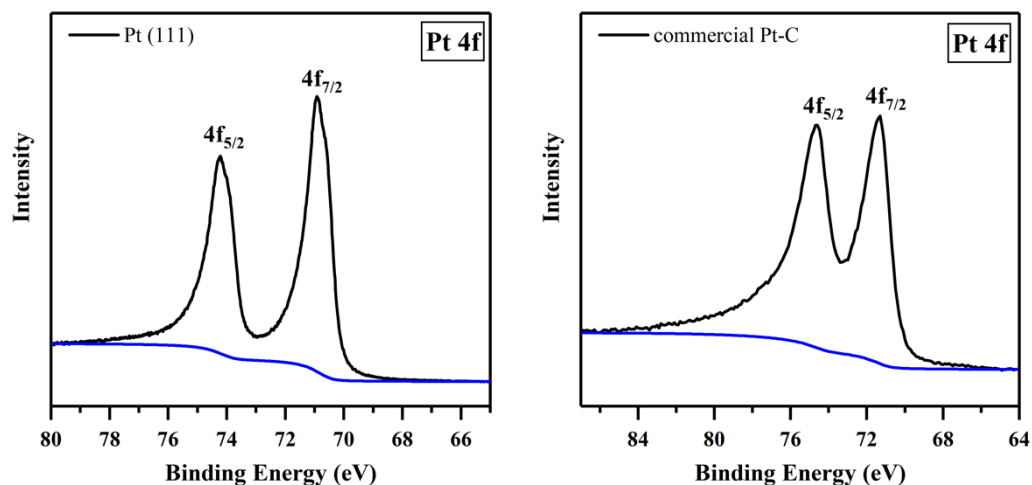


Figure A.1 Pt4f XPS graphs for Pt (111) as a reference and commercial C-Pt with baselines

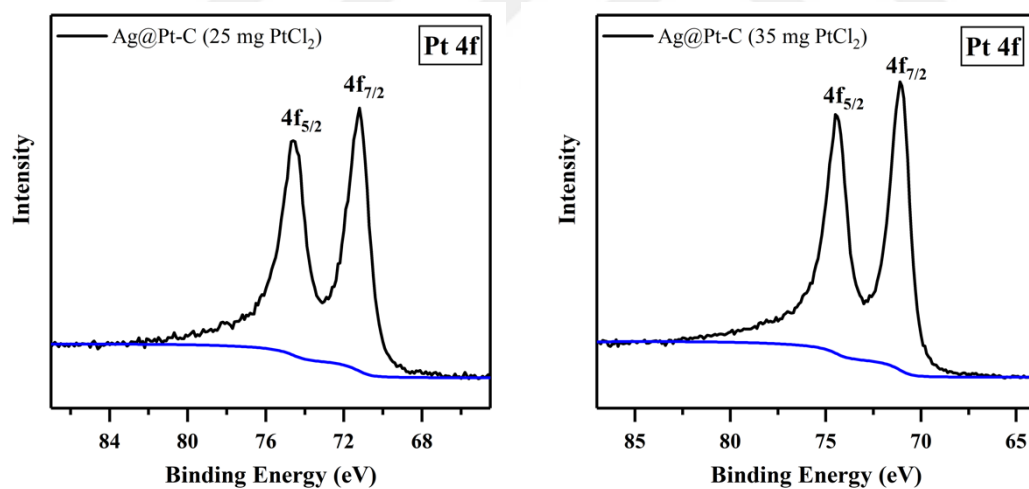


Figure A.2 XPS Pt4f graphs for C-Ag/Pt (25 mg and 35 mg PtCl_2) with baselines

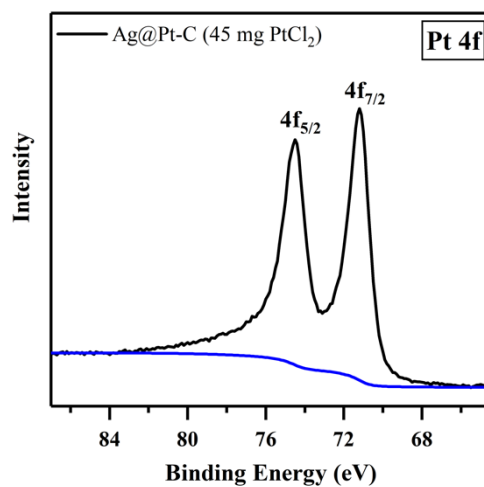


Figure A.3 XPS Pt4f graphs for C-Ag/Pt (45 mg PtCl₂) with a baseline

Appendix III – Calculations for XRD Peak Positions for Pt and Ag

Table A.2 XRD Peak Positions (2 θ values) for Pt and Ag

Element	R (nm)	a (nm)	hkl	d _{hkl} (nm)	sin(θ)	2 θ _{calculated}
Pt	0.139	0.393	111	0.227	0.339	39.68
			200	0.197	0.392	46.14
			220	0.139	0.554	67.31
			311	0.119	0.650	81.06
			331	0.090	0.854	117.31
Ag	0.144	0.407	111	0.236	0.327	38.12
			200	0.204	0.377	44.31
			220	0.144	0.533	64.46
			311	0.123	0.625	77.42
			222	0.118	0.653	81.56

Sample Calculation for 2 θ [11]

Sample calculations were made for Pt (200).

$$a = 2\sqrt{2}R \text{ for FCC}$$

$$\therefore a = 2\sqrt{2} \times (0.139 \text{ nm}) = 0.393 \text{ nm}$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$\therefore d_{hkl} = \frac{0.393 \text{ nm}}{\sqrt{2^2 + 0^2 + 0^2}} = 0.197 \text{ nm}$$

From Bragg's Law in equation (16),

$$\sin(\theta) = \frac{\lambda_{\text{Cu-K}\alpha}}{d_{hkl}} \quad \text{where } \lambda_{\text{Cu-K}\alpha} = 0.154 \text{ nm}$$

$$\sin(\theta) = \frac{0.154 \text{ nm}}{0.197 \text{ nm}} = 0.392$$

$$\therefore 2\theta = 2 \times \arcsin(0.392) = 46.14^\circ$$

Appendix IV – ECSA Graphs

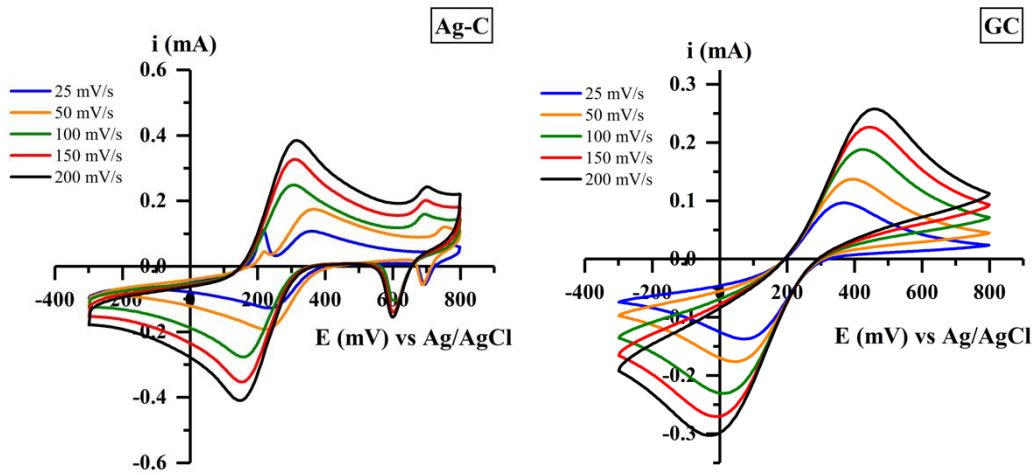


Figure A.4 ECSA for C-Ag and glassy carbon electrode

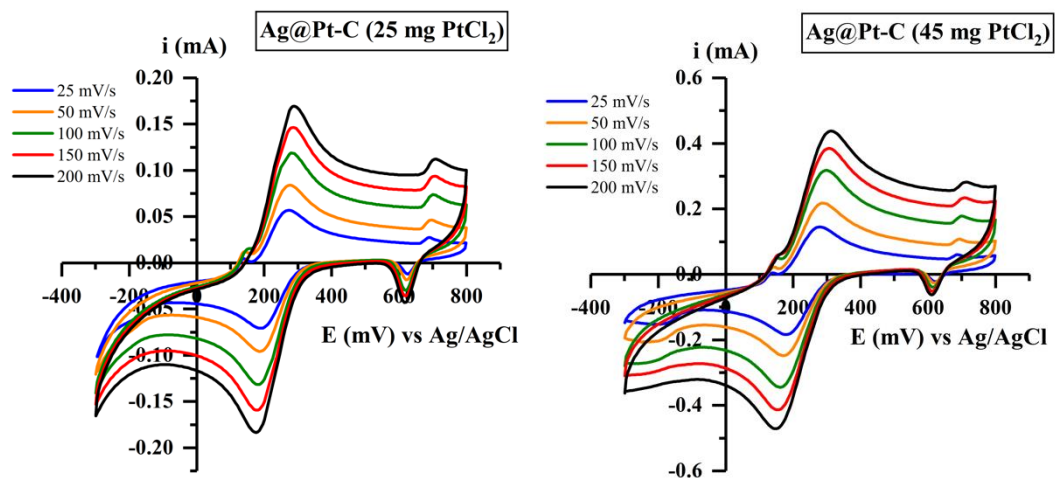


Figure A.5 ECSA for C-Ag/Pt (25 mg and 45 mg PtCl_2)

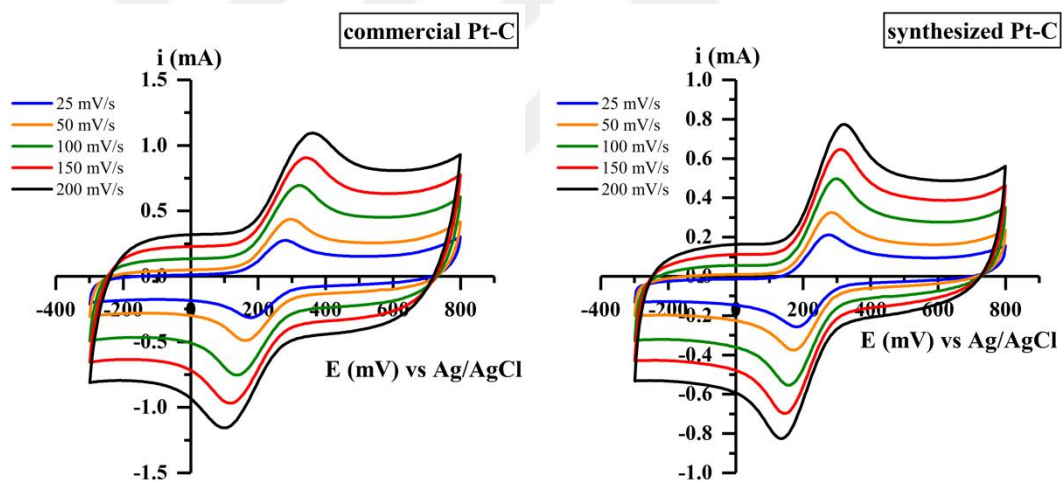


Figure A.6 ECSA for commercial C-Pt and synthesized C-Pt

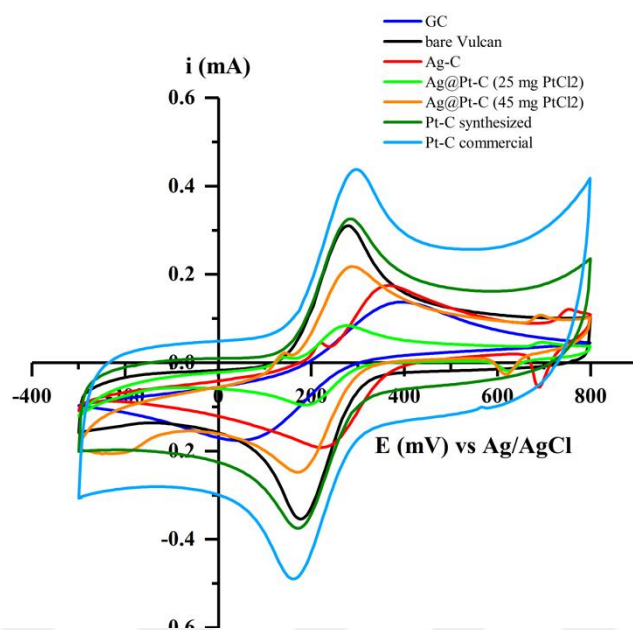


Figure A.7 ECSA for all samples at 50 mV/s