

Dedicated To

My dearest friend

Nasim Rahmanifar

**APPLICATION OF COVALENT ORGANIC
FRAMEWORK BASED ON PORPHYRIN AND
CUCURBIT[6]URIL AS A BIFUNCTIONAL
ELECTROCATALYST FOR HYDROGEN AND
OXYGEN EVOLUTION**

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By
Yasaman Sheidaei
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Application Of Covalent Organic Framework Based On Porphyrin And
Cucurbit[6]uril As A Bifunctional Electrocatalyst For Hydrogen And Oxygen
Evolution

By Yasaman Sheidaei

January 2021

We certify that we have read this thesis and that in our opinion it is fully adequate, in
scope and in quality, as a thesis for the degree of Master of Science.



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ABSTRACT

APPLICATION OF COVALENT ORGANIC FRAMEWORK BASED ON PORPHYRIN AND CUCURBIT[6]URIL AS A BIFUNCTIONAL ELECTROCATALYST FOR HYDROGEN AND OXYGEN EVOLUTION

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There is great apprehension about consumption of fossil fuels as well as the corresponding environmental issues which has evoked supreme efforts worldwide to develop clean and sustainable energy sources. Electrocatalytic water splitting producing both hydrogen and oxygen gas has shown considerable potential for energy conversion as hydrogen can meet the requirements for future energy demands. Hence it is of utmost importance to introduce novel electrocatalysts to overcome energy barriers for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Here this thesis highlights the synthesis and characterization of a novel supramolecular assembly of cucurbit[6]uril and porphyrin and also examines its electrocatalytic activity toward both HER and OER. Electrochemical studies such as linear sweep voltammetry, chronoamperometry, chronopotentiometry, electrochemical impedance spectroscopy were performed to investigate the activity of the catalyst. The structural and morphological properties of sample were also studied using scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FT-IR). It was observed that the catalyst was able to show excellent electrocatalytic activity with onset potentials of -0.25 V (for HER) and 1.6 V (for OER) while producing 18.7 and 14.92 mmol.gr⁻¹.hr⁻¹ hydrogen and oxygen gas with faradaic efficiencies of 85% and 99%, respectively.

Key words: Covalent organic framework, water-splitting, bifunctional electrocatalyst for hydrogen and oxygen evolution, cucurbituril, porphyrin.

ÖZET

HİDROJEN VE OKSİJEN EVRİMİ İÇİN BİFONKSİYONEL ELEKTROKATALİZÖR OLARAK PORFİRİN VE KÜKÜRBİT[6]ÜRİL BAZLI KOVALENT ORGANİK YAPININ UYGULANMASI

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Fosil yakıtların tüketiminin sonucunda ortaya çıkan çevre sorunlarının yarattığı endişe sebebiyle, temiz ve sürdürülebilir enerji kaynakları geliştirmek için dünya çapında büyük çabalar sarf edilmektedir. Hem hidrojen hem de oksijen gazı üreten elektrokatalitik su ayrıştırması yöntemi, hidrojenin gelecekteki enerji taleplerini karşılayabilmesinden dolayı enerji dönüşümü için önemli bir potansiyel göstermiştir. Bu nedenle, hidrojen evrimi reaksiyonu (HER) ve oksijen evrimi reaksiyonu (OER) için enerji engellerinin üstesinden gelmek amacıyla yeni elektrokatalizörlerin tanıtılması son derece önemlidir. Bu tez, kükürbüt[6]üril ve porfirinin yeni bir supramoleküler birleşiminin sentezini ve karakterizasyonunu vurgulamakta ve aynı zamanda hem HER hem de OER'ye yönelik elektrokatalitik aktivitesini incelemektedir. Katalizörün aktivitesini incelemek için lineer süpürme voltametri, kronoamperometri, kronopotansiyometri, elektrokimyasal empedans spektroskopisi gibi elektrokimyasal çalışmalar yapılmıştır. Numunenin yapısal ve morfolojik özellikleri, taramalı elektron mikroskobu (SEM), X-ışını kırınım analizi (XRD), X-ışını fotoelektron spektroskopisi (XPS) ve Fourier-dönüşümlü kızılötesi spektroskopisi (FT-IR) kullanılarak da incelenmiştir. Katalizörün, sırasıyla % 85 ve % 99 faradaik verimlerle 18.7 ve 14.92 mmol.gr⁻¹.hr⁻¹ hidrojen ve oksijen gazı üretirken, -0.25 V (HER için) ve 1.6 V (OER için) başlangıç potansiyelleriyle mükemmel elektrokatalitik aktivite gösterebildiği görülmüştür.

Anahtar kelimeler: kovalent organik yapının, elektrokatalizör, su ayırma, hidrojen ve oksijen için bifonksiyonel elektrokatalizör, kükürbütiril, porfirin.

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Chapter 1

Introduction

1.1 Water splitting

Overall water splitting reaction is presented below which consists of two half reactions of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER):



This required electricity can be afforded through sustainable and non-sustainable sources of energy. Photo-electrocatalysis is a well-known method in which photon energy, the most abundant energy source, is absorbed by the photocatalyst and then converted to chemical energy[1]. General process is shown in Fig. 1a. Whereas electrocatalysis uses electricity to split water molecules.

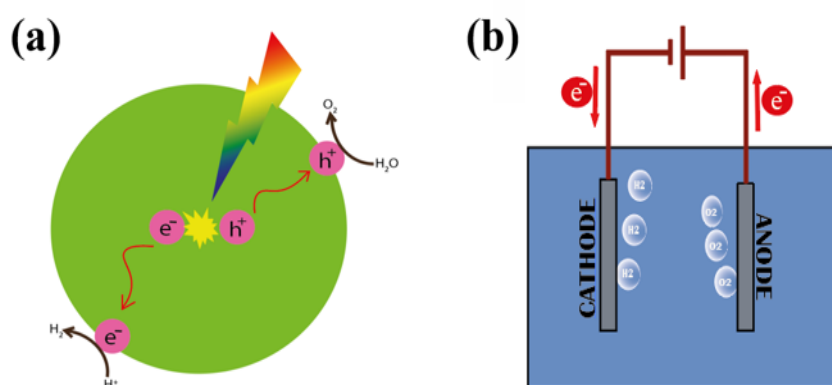


Figure 1-1- (a) general process in photocatalytic water splitting induced by light irradiation, (b) overview of electrocatalytic water splitting cell.

Regardless of the method used to provide this energy, thermodynamic rules state that a potential of 1.23 V can lead to water splitting under standard conditions which is

equivalent to Gibb's free energy of 237.1 kJ.mol⁻¹. But due to poor kinetics of hydrogen evolution (HER) and oxygen evolution (OER) reactions, higher potential is required to drive these reactions at a measurable current density. Hence the required potential for water splitting can be calculated from equation below:

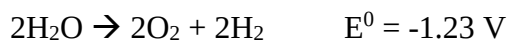
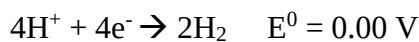
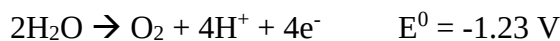
$$V_{\text{overall}} = 1.23 + |\eta_{\text{HER}}| + \eta_{\text{OER}} + \eta_{\text{IR}} \quad (\text{Equation 1-1})$$

Where V_{overall} is the required potential for overall water splitting, η_{OER} and η_{HER} are the overpotentials (entailed additional potentials) for OER and HER, respectively. The solution resistance can also increase the required potential represented by η_{IR} . In general, these extra imposed potentials ($|\eta_{\text{HER}}| + \eta_{\text{OER}} + \eta_{\text{IR}}$) can be defined as the energy loss under non-standard conditions[2]. Electrocatalysts are used to increase the rate of electron transfer, contributing to facilitated redox reactions[3]. These eventually result in lower overpotential and higher efficiency in energy conversion. However, precious metals (e.g., Pt for HER and Ru and Ir for OER) are incorporated in the most common electrocatalysts for acidic electrolytes[4]. Their scarcity as well as high cost have provoked enormous research for alternative electrocatalysts with non-noble metal or earth-abundant elements with adequate activity toward water splitting under reduced overpotentials[5]. Many examples of these electrocatalysts like chalcogenides[6], metal alloys and carbides can be found in the literature[7][8]. For alkaline solutions, electrocatalysts containing transition metals (e.g., Ni for HER and stainless steel for OER) in the form of metal oxides[9] or hydroxides[10][11] are prevalent[12].

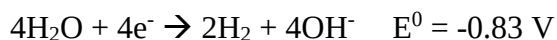
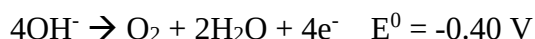
1.1.1 Hydrogen Evolution Reaction (HER)

As it was mentioned earlier, electrocatalytic hydrogen production from water splitting has been considered as a promising technique to pave the way for clean hydrogen fuel. Depending on whether water splitting is occurring in acidic or basic medium, it can follow either of the following two half-reactions:

In acidic solution:



In basic solution:



Metal catalysts have faster activity toward HER in acidic medium, in comparison with their behavior in alkaline solutions. Slow water dissociation step in alkaline medium is responsible for the lower activity of catalysts, which overall weakens the kinetics of HER in this type of electrolyte.

1.1.1.1 Hydrogen as fuel

Known as the simplest and lightest element in the periodic table, hydrogen is a crucial element in many structures, from organic compounds to water and prebiotics. Mostly it has no odour, colour or taste and its condensation point is at 20.26 K. It shows a high reactivity at elevated temperatures and can be used to free metals from metal oxides or metal chloride. In hydrogenation reactions, hydrogen would react with alkenes to produce alkanes (e.g., hydrogenation of ethylene to ethane)[13].

Industrial Revolution was the starting point of intensive use of fossil fuels such as coal, oil and gas. As we became more dependent on these resources, the imperative issues, i.e., the fast depletion of fossil fuels and the excessive greenhouse gas emissions, emerged indicating the vital need for renewable sources of energy[14]. Based on extraordinary increase in energy demand as well as population, it is predicted that there will be a sharp increase of 56% from 2010 to 2040[15].

Hydrogen is a promising candidate as clean energy source. Combustion or electrochemical conversion of hydrogen with oxygen produces energy and water vapor, meaning there is no carbon emissions which makes hydrogen as a clean source of energy. Explosion is a danger of hydrogen leakage due to high reactive character. However, applying safety controls would make it as appropriate as other fuels to get advantage of physical properties of this element as an energy carrier.

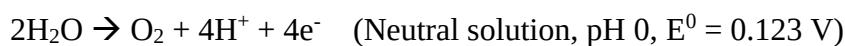
Hydrogen possesses the widest range of flammability of 4% to 75% as well as the highest heating value of 52,000 Btu/lb. Comparing the range of flammability of hydrogen with gasoline (1%-7.6%) proves the fact that hydrogen would decrease the combustion temperature of the lean mixtures, and consequently the efficiency of the hydrogen engines is better than gasoline engines. This decline in the combustion temperature can be beneficial in subduing nitrogen oxide emissions. Furthermore, the efficiency of 57 million tons of hydrogen is equal to 170 million tons of oil. Other properties such as high diffusivity, ease of combustion, and low viscosity are effective factors in considering hydrogen as a convenient substitution for non-renewable fuels[13]. Table 1([16]) compares some properties of hydrogen with other fuels.

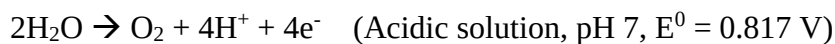
Table 1-1- Properties of hydrogen as fuel with other fuels

Fuel	Gravimetric energy density (MJ.kg-1)	Volumetric energy density (MJ.I-1)	Flammability limits (vol%)	Explosive limits (vol%)
Hydrogen compared 200 bar	120	2.1	-	-
Hydrogen liquid	120	8.4	4-75	18.3-59.0
Methanol	19.7	15.7	6-36.5	6-36
Petro	42	31.5	1-7.6	1.1-3.3
Diesel	45.3	35.5	-	0.6-7.5
Kerosene	43.5	31.0	-	0.7-5

1.1.2 Oxygen Evolution Reaction (OER)

Oxygen evolution reaction is actually considered as the bottle-neck for water splitting as high amount of energy is essential to drive this reaction[17]. Like HER, the pH of electrolyte can affect the mechanism OER follows. As it is shown below, performing OER in an alkaline electrolyte the oxidation of hydroxyl groups leads to oxygen generation. Whilst oxygen is produced through oxidizing water molecules in acidic and neutral media[18].





In all three electrolytes, four electrons are involved to make OER happen. This can be translated to presence of more than one intermediate during the process which gives rise to the high energy demand and consequently the sluggish kinetics of OER[17]. Hence electrocatalysts are employed to overcome this huge energy barrier and provide acceptable current densities at lower cost of overpotential.

So overall HER and OER can follow the each of the steps illustrated in Figure 1-2 performing in an acidic electrolyte.

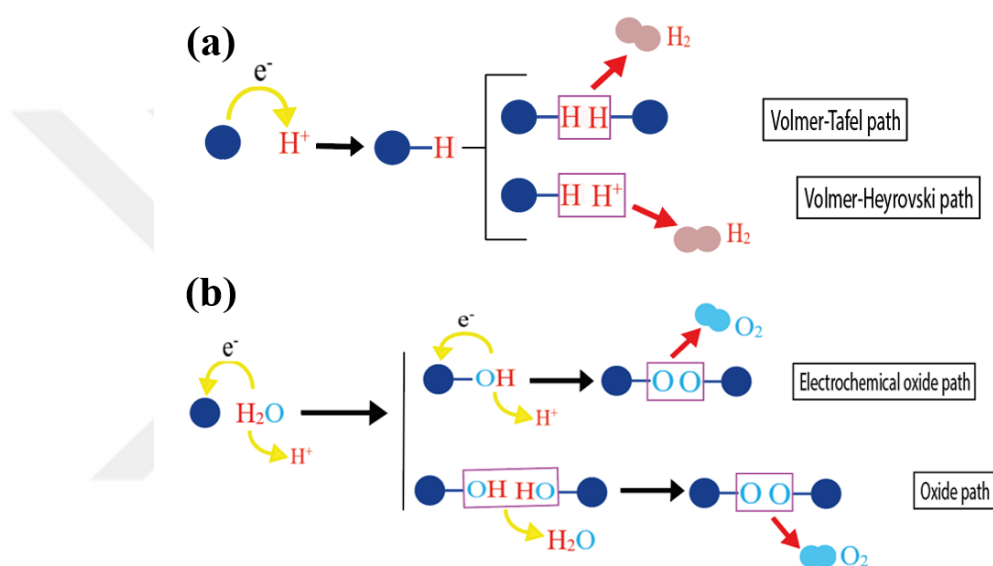


Figure 1-2- Proposed pathways for (a) HER and (b) OER in acidic medium (Reproduced from [19])

1.1.3 Porphyrins

Organic materials have been attracted many attentions in recent decades for optoelectronic and catalysis applications. Delocalized π -electrons can attribute to easier modulating the molecular structure and functions through applying proper design procedure and tailoring[20]. One of the important superiorities of organic polymers is their tenability of their light-absorption properties and their solution processability[21]. Covalent organic polymers with accurate tailoring location of active sites, high porosity, as well as stability in acidic and basic medium[22][23] have also shown great potentials in catalysis.

Porphyrins are important group of organic macrocycles. They are responsible for photosynthesis and electron transfer reactions in the nature[24]. Unique characteristics such as strong light absorption, ease of chemical modification, planar structure, and high stability have made them attractive candidates for various applications[20]. There are many reports of facile synthesis of porphyrins by sulphonation, carboxylation or alkylation of N-pyridyl compounds[25].

Porphyrins as tetrapyrrole derivatives contain four pyrrole rings conjugated by methine groups (-CH=). Redox and optical properties of these structures stem from 18 π -electrons as their electronic center. Benefiting from these features and their tendency to self-assemble into ordered structures, various novel materials can be designed to imitate the natural behavior of porphyrins and being employed in solar cell[26], electrocatalytic water splitting[19], field-effect transistors, organic semiconductor fields.

Based on the central structure of porphyrins, they are divided into two groups of free-base porphyrins and metalloporphyrins. In the case of free-base porphyrins, there are two hydrogen atoms in the center. It is proposed that pyrrolic nitrogen atoms are considered as catalytic sites at which protonation presumably happens[27]. These nitrogens bring the protons close enough that can ultimately lessen the activation energy required for transition state of H-H binding[28]. Adjusting properties like π -electronic conjugation and proper active side groups, alongside exploiting novel molecular designs give rise to development of new advance materials with electrochemical responsiveness[29]. Manton and co-workers reported electrocatalytic activity of a series of free-base porphyrin complexes. In this regard, tetraphenyl-porphyrin (TPP) complexes with different substituents were deposited on glassy carbon electrode and their activity toward HER was studied in aqueous buffer solution. It was observed that MeOTPP exhibited the highest electrocatalytic activity with faradaic efficiency of 90% as well as turn-over number¹ (TON) of up to 250000 with more than six hours stability. This was almost the first report on modification of the electrode surface with a metal-free porphyrin showing improved electrocatalytic HER activity[27].

¹ Turnover number is obtained by total number of H₂ produced per moles of electrocatalyst.

Meanwhile two protons in the porphyrin ring can be substituted by a metal. Deprotonated porphyrins are capable of coordinating almost all transition metal ions which produces a four-coordinate structure. Due to both the exposed axial unoccupied positions of metal ion, the square planar Me-N₄ moieties represent idea electrocatalytic active centers[30][31]. The absorption spectra of porphyrins can be manipulated by the metal as a result of interaction between electrons from metal and from the ring[32]. There has been a growing interest in metalloporphyrins in various fields from enzymatic reactions to energy transduction systems. Upon applying adequate potential, these porphyrins can be served as electrocatalysts to convert protons to hydrogen gas and carbon dioxide to carbon monoxide[33].

There are many reports on application of metalloporphyrins as HER electrocatalysts in the literature. As an example, Canales and co-workers[34] worked on electrocatalytic activity of metalloporphyrins (M-OEP, M=Co(II), Cu(II), Zn(II), Ru(II), Fe(II) and Ni(II), OEP= 2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine) deposited on modified glassy carbon electrode for hydrogen production at pH 7. Covalent modification by sodium hydroxide and reaction with 4-aminopyridine (4AP) was applied to glassy carbon electrode that provided perfect platform for π -stacking of metalloporphyrins assemblies. The π -stacking improves the electron transfer between electrode and active sites of metalloporphyrins. GC+4AP+Co(II)OEP with turn-over number of 6.4×10^3 showed the highest activity toward H₂ evolution.

Metalloporphyrins are also widely used in OER. A Co(II)-porphyrin/pyrene-based conjugated microporous polymer Co-MPPy-1 was successfully synthesized which exhibited efficient O₂ evolution activity in alkaline medium[35]. In this regard, solution-phase Pd-mediated Suzuki cross-coupling reaction was applied to synthesize pyrene/porphyrin donor-acceptor conjugated polymeric bilayer heterojunction with Co(II) as active sites for oxygen production in 1 M NaOH. Without any thermal activation, CMP was able to produce 10 mA.cm⁻² only at the cost of 420 mV. Turnover number for OER was calculated to be 0.43 s⁻¹. Efficient charge transfer in the π -conjugated polymeric structure may be responsible for this high activity.

1.1.4 Cucurbiturils

Host-guest chemistry has had significant influence on fabrication of supramolecular systems as inclusion of molecule (guest) into the cavity of molecular container (host) can lead to new chemical transformations applicable in various fields, particularly in biomedical application.

Cucurbit[n]urils (CB[n]s) have received rising attention in recent decades. These groups, mostly including CB[5], CB[6], CB[7], CB[8] and CB[10], can be synthesized through condensation reaction of glycoluril and formaldehyde catalyzed by acid which results in glycolurils linked by methylene bridges[36]. Although CB[n]s have the same height of 9.1 Å, cavity size, annular and equatorial widths differ with number of repeating units[37]. Cucurbit[6]uril (CB6) was synthesized by Behrend and coworkers[38] in 1905 and its molecular structure was revealed almost 76 years later by Mock and coworkers[39]. It is known as “parent cucurbituril” that includes six glycolurils embedded. Variation in reaction conditions caused isolation of other CBs with 5, 7, 8 and 10 glycoluril units. Symmetrical structure as well as hydrophobicity of their cavity are among important features of cucurbit[n]urils. In addition to this, carbonyl groups on the periphery of cavity are negatively charged. Using electrostatic maps it was observed that carbonyl oxygens possess high electron density, which can justify the cation-receptor behavior of CBs[40]. There are various congeners of CBs with different cavity sizes, binding affinity and improved solubility in the literature. These structures have exhibited outstanding potential in catalysis[41][42][43], drug delivery[44][45], fluorescence sensing[46] and etc.

Despite all interesting properties of porphyrins, their π -conjugated structures can drag them to aggregate in aqueous solution or solid state which can in turn perturb their water solubility. Cucurbiturils assemblies with porphyrin is proposed to be a constructive solution[28]. Water soluble [5]rotaxane and [5]pseudorotaxane based on cucurbit[6]uril and anchored to a mesotetraphenyl porphyrin was the first work reported on these assemblies[47].

1.2 Electrochemical parameters and measurements

1.2.1 Nernst equation

The potential of a half-reaction happening on an electrode can be related to its standard electrode potential, E° , using the Nernst equation:

$$E = E^\circ - \frac{RT}{nF} \sum \nu_i \ln a_i \quad (\text{Equation 1-2})$$

Where a_i is activity, ν_i is the stoichiometric number. Standard electrode potential is reported relative to the normal hydrogen electrode (NHE) and all the activities are equal to one.

Instead of activities, concentrations (c_i) also can be employed as: $a_i = \gamma_i c_i$ with γ_i representing the activity coefficient of species i . Hence equation above can be rewritten as:

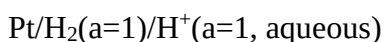
$$E = E^{\circ'} - \frac{RT}{nF} \sum \nu_i \ln c_i \quad (\text{Equation 1-3})$$

$E^{\circ'}$ is formal potential which contains logarithmic activity and E° , hence making it a medium-dependent parameter.

The Nernst equation can be applied when the electrode reactions reach equilibrium at the electrode surface. These electrode reactions are then called Nernstian or reversible as they obey thermodynamic relations. Obviously these terms are interrelated with the given time for the redox reactions to reach equilibrium.[48]

1.2.2 Potential

In an electrochemical cell, the potential of a working electrode is measured with respect to a reference electrode. The reference electrode have a constant potential which cannot be changed during a reaction, making them non-polarizable. Hence any changes in the potential is ascribed to the energy changes of electrons on the working electrode. Standard hydrogen electrode (SHE), or normal hydrogen electrode (NHE), is the primary reference electrode which is:



The activity of the all components is one.

The other common reference electrodes are silver-silver chloride (Ag/AgCl/KCl, saturated in water) and saturated calomel electrode (SCE) (Hg/Hg₂Cl₂/KCl, saturated water) with a potential of 0.197 and 0.242 V vs. NHE, respectively.

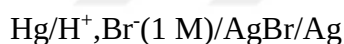
For instance, when there is Ag/AgCl reference electrode in an electrochemical cell, the potential of electrode (vs. RHE) in an electrolyte with a specific pH can be calculated as:

$$E \text{ (vs. RHE)} = E_{(\text{Ag/AgCl/KCl (sat.)})} + 0.059\text{pH} + E_{(\text{Ag/AgCl/KCl (sat.)})}^0 \quad (\text{Equation 1-4})$$

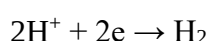
Where E is the potential of the electrode with respect to RHE, $E_{(\text{Ag/AgCl/KCl (sat.)})}$ is the potential measured by the potentiostat, and $E_{(\text{Ag/AgCl/KCl (sat.)})}^0$ is the standard potential (0.197 V)[49].

1.2.3 Overpotential

Let's consider we have an electrochemical cell as below:



Upon applying a reducing potential, one would expect to observe H₂ evolution reaction (reaction below) on the mercury electrode.



However, when a negative potential is applied, in spite of thermodynamics envision, no current flows and consequently, no H₂ gas is evolved. In order to make this reaction happen, the potential must be driven to more negative values. Comparing Pt and mercury as the venue for hydrogen evolution electrode, Hg possesses much lower heterogeneous rate constant, meaning that higher electron energy, in terms of potential, is required to have reaction 1 at a considerable rate. This added potential beyond the thermodynamically predicted potential provoking a reaction at a particular rate is known as overpotential (η). In other words, overpotential can be defined as the increased thermodynamic driving force for electrochemical process. Going back to the comparison between Pt and Hg electrodes, it can be said that Hg demands a higher overpotential for H⁺/H₂ reaction.

For reduction reactions, overpotentials are negative. While having a positive overpotential can contribute to an oxidation reaction. For a given reaction, overpotential can provide an appropriate platform to evaluate the efficacy of a catalyst/electrode. In this regard, the lower the overpotential (regardless of its sign), the better the catalyst is for that specific reaction [49][50].

Overpotential for hydrogen and oxygen evolution reactions (HER and OER, respectively) can be calculated as:

$$\eta = E_{\text{applied (vs. RHE)}} - E^0_{\text{(vs. RHE)}} \quad (\text{Equation 1-5})$$

Where $E_{\text{applied (vs. RHE)}}$ is the applied potential vs. RHE

$E^0_{\text{(vs. RHE)}}$ is the reversible potential (0 V vs. RHE for OER and 1.23 V vs. RHE for OER).

1.2.4 Linear sweep voltammetry

Linear sweep voltammetry (LSV) is one of the most common electrochemical techniques for examining redox reactions. This method can be utilized for both organic and inorganic materials. Basically the working electrode potential is changed linearly from E_1 to a more negative (reduction, cathodic sweep) or more positive (oxidation, anodic sweep) potential of E_2 with a specific scan rate of v (V.s^{-1}). The sign of v determines the direction of reaction toward reduction or oxidation. Hence the potential of the electrode at time t is given by:

$$E_t = E_i \pm vt \quad (\text{Equation 1-6})$$

Where E_t is the applied potential at t , and E_i is the initial potential. The resultant current from such potential ramp shows an exponential behavior.

1.2.5 Chronoamperometry (CA)

One of the techniques used to examine the activity as well as durability of an electrocatalyst is chronoamperometry experiment which can be defined as measuring current response as a function of time upon applying a square-wave potential to a

working electrode[51][52]. In this measurement, only diffusion contributes to the mass transfer and as the time passes, deficiency of reactant results in expansion of diffusion layer. The reactant depletion can be understood from decreasing slope of concentration gradient (Figure 1-3). Consequently, the value of current would decay in time by:

$$i(t) = \frac{nFCA D^{1/2}}{\pi^{1/2} t^{1/2}} \quad (\text{Equation 1-7})$$

where n, F, C, A, D and t are the number of electrons, Faraday's constant, the concentration, electrode area, diffusion coefficient and time, respectively. This equation is known as Cottrell equation.

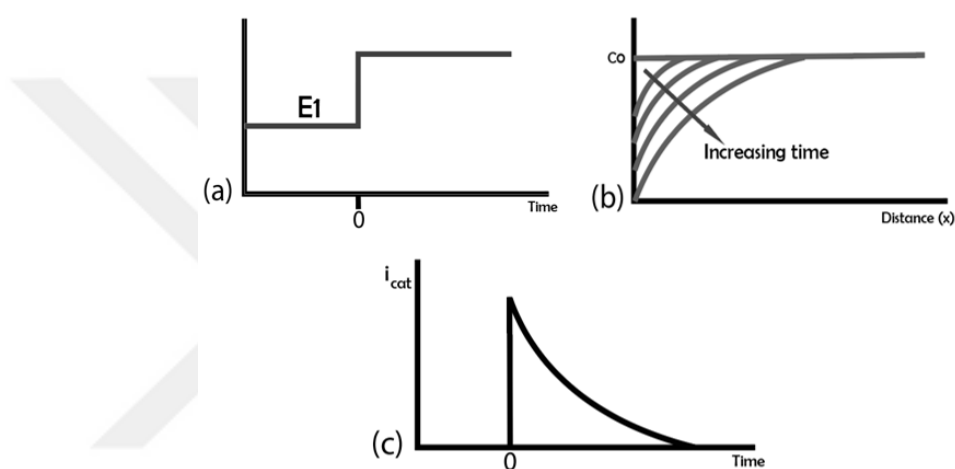
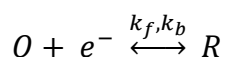


Figure 1-3- (a) Step waveform applied to the working electrode, (b) Concentration gradient of reactant in various time during the reaction, (c) Current response of the system with respect to time. (Reproduced with permission from [49])

1.2.6 Tafel equation

Let's consider a simple redox reaction:



Where k_f (cm.sec⁻¹) and k_b (cm.sec⁻¹) are the heterogeneous rate constants of forward and backward reactions, respectively. These constants can be written in terms of the standard heterogeneous rate constant (k^0) as:

$$k_f = k^0 e^{-\alpha f(E-E^0)} \quad (\text{Equation 1-8})$$

$$k_b = k^0 e^{(1-\alpha)f(E-E^0')} \quad (\text{Equation 1-9})$$

Here $f=F/RT$, F is Faraday's constant (C/mol), α is dimensionless transfer coefficient in range of 0 to 1 which is often estimated to be 0.5.

Having i_c (A), the cathodic current as the result of the forward reaction and i_a (A), known as the anodic current due to backward reaction, the overall current passes through the system is equal to:

$$i = i_c - i_a \quad (\text{Equation 1-10})$$

In which each of the cathodic and anodic current can be calculated by the corresponding rate constants as below:

$$i_c = F A k_f C_O(0, t) \quad (\text{Equation 1-11})$$

$$i_a = F A k_b C_R(0, t) \quad (\text{Equation 1-12})$$

Where A is the electrode area (cm^2), C_o and C_R are the O and R concentrations at the electrode surface (mol/cm^3) at the time t (sec). By combining above equations substituting them in equation 1-10, there is:

$$i = F A k^0 [C_O(0, t) e^{-\alpha f(E-E^0')} - C_R(0, t) e^{(1-\alpha)f(E-E^0')}] \quad (\text{Equation 1-13})$$

In this equation current of the system is related to the potential and can be considered as a basis for heterogeneous electrode kinetics.

At equilibrium, the current flowing in the cathodic direction is exactly the same as the anodic current leading to have no net current in the cell. In other words:

$$i_a = i_c = i_0 \quad (\text{Equation 1-14})$$

where i_0 is the exchange current density and can be written as a function of k^0 and the bulk concentration of O (C_O^*) and R (C_R^*) species.

$$i_0 = F A k^0 C_O^{*(1-\alpha)} C_R^{*\alpha} \quad (\text{Equation 1-15})$$

Equations 1-15 and 1-13 can be used to relate current to overpotential (η [V]) through the equation below:

$$i = i_0 \left[\frac{C_O(0,t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha) f \eta} \right] \quad (\text{Equation 1-16})$$

In a well-stirred solution it can be concluded that the concentration of the species are equal in every point and this leads to:

$$C_O(0,t) = C_O^* \quad (\text{Equation 1-17})$$

$$C_R(0,t) = C_R^* \quad (\text{Equation 1-18})$$

So equation 1-16 can be simplified to Butler-Volmer equation:

$$i = i_0 [e^{-\alpha f \eta} - e^{(1-\alpha) f \eta}] \quad (\text{Equation 1-19})$$

In this equation it is assumed that the system is not mass-transfer limited and this is true for the solution when it is perfectly stirred. At large overpotentials (either positive or negative values), one of the exponential terms in equation 1-19 can be neglected and by rearranging it, the overpotential can be written as a function of current which is known as Tafel equation[49][53]:

$$\eta = \frac{RT}{\alpha F} \ln i_0 - \frac{RT}{\alpha F} \log i \quad (\text{Equation 1-20})$$

Tafel plot exhibits the logarithmic dependence of the current density to overpotential. The polarization curves are utilized to plot $\log i$ against η for cathodic and anodic branches. It is worth mentioning that as η goes to very small values (< 50 mV), the concentration profile would differ at electrode surface, resulting from the fact that with considering the cathodic current, the anodic reaction contributes more than 1% of the current (or vice versa). Hence the Tafel plot would significantly deviate from linearity as η is decreased to zero. On the other hand also Tafel equations can be applied if there is no impact of mass transfer on the current of the electrochemical cell. Then for very large values of η ($> \text{few hundred mV}$), where the mass-transfer limitations come into play, Tafel relations cannot be applied[49][53].

Tafel equation[54] can be written as:

$$\eta = a + b \log |i| \quad (\text{Equation 1-21})$$

$$b = \frac{RT}{n\alpha F} \quad (\text{Equation 1-22})$$

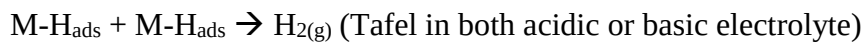
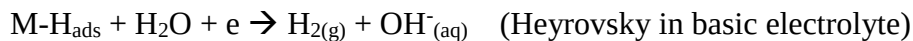
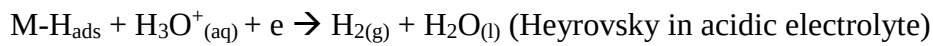
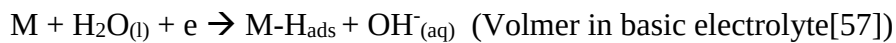
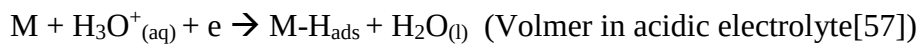
Where b is Tafel slope and a is Tafel intercept. As it was mentioned earlier, α is transfer coefficient and n shows the number of electrons. Tafel slope is an implicit property of the catalyst which provides a useful basis to evaluate the efficiency of the electrocatalysts by comparing how fast the system would response to overpotential changes in terms of current. The smaller the Tafel slope is, the faster HER rate boosts at elevated overpotentials[55]. There are several parameters affecting the Tafel slope, including reaction route, electrode modification procedure, catalyst preparation and adsorption condition of the active sites and etc. Assuming that $\alpha=0.5$, $T=298.15$ and $n=1$, Tafel slope would be equal to:

$$\frac{2 \times 2.23 RT}{F} = 118 \text{ mV/dec} \quad (\text{Equation 1-23})$$

Equation 20-2 can be also used to obtain exchange current density. Exchange current density is actually the current flowing through the system in both forward and backward reactions at equilibrium state. In other words, as electrocatalysts facilitate the electron transfer in electrochemical reactions, exchange current density can provide a comprehensive insight of the electron transfer rate. The high exchange current density implies that there is lower energy barrier for the electrons to move which yields to higher current densities in lower overpotentials. Among the catalyst for hydrogen evolution reaction, Pt electrode shows the highest exchange current density[56].

We can summarize that an efficient electrocatalyst reveals a small Tafel slope accompanied with a high exchange current density.

HER proceeds through the following reactions:



The first reaction is so-called Volmer reaction which is a discharge reaction. In this step H_3O^+ is adsorbed to the active site of the catalyst and forms M-H. Then the hydrogen can be liberated through either Heyrovsky or Tafel reaction. In Heyrovsky reaction, as

an Eley-Reidel type reaction, occurs when the adsorbed H reacts with another proton and an electron. Instead of this reaction, two adsorbed atoms can recombine and produce H_2 through Tafel reaction which is a Langmuir-Hinshelwood type reaction. Overall hydrogen evolution would follow either Volmer-Heyrovsky or Volmer-Tafel mechanism. Tafel analysis can be applied to determine the reaction mechanism as well as the rate-determining step (rds) of an electrochemical process. When the Volmer step is considered as the rds, materials providing more edges and cavities in their surface structure, can improve the electron transfer and subsequently increase the electrolysis spots on the electrode. While physical properties such as surface roughness can be practical to either increase the reaction area or inhibiting bubbles from growing, when Tafel or Heyrovsky is rds.[58]. However, the uncertainties resulting from the complexity of the reactions at the electrode surface and kinetic data interpretation from experimental results make it complicated to deduce the reaction pathway[59].

1.2.6.1 Interpretation of Tafel slope

There are several reports on application of porphyrin complexes as electrocatalysts for HER. Huang and the coworkers[60] worked on a cobalt porphyrin structure ([tetrakis (N-methylpyridyl) porphyrinato] cobalt) accompanied with electrochemically reduced graphene oxide through layer-by-layer assembly method and examined its electrocatalytic activity toward HER in alkaline media for various deposition cycles. The electrocatalysts showed the Tafel slopes of about 114 mV/dec which suggests a Volmer-Heyrovsky mechanism for this system.

In another study, HER activity of a bifunctional electrocatalyst derived from copper porphyrin-based mesoporous polymer was studied in basic electrolyte (1.0 M KOH). Here the working electrode was a glassy carbon electrode coated with an ink prepared from Cu-CMP samples after pyrolysis reaction at various temperatures. By plotting Tafel plots from the polarization curves, it was calculated that the Tafel slope is about 135 mV.dec⁻¹. According to this slope, it can be concluded that the adsorption step (Volmer) is the r.d.s during hydrogen evolution process[61].

Using Ni foam as an electrocatalyst in an acidic medium of H_2SO_4 for hydrogen evolution was performed by Lu and coworkers. After fitting the linear portion of the

polarization curve to Tafel equation, the slope was about 100.6 mV.dec. Also the polarization curve was recorded for a platinum sheet for comparison. The Pt had smaller Tafel slope of 30.6 mV.dec, meaning that it followed the Tafel reaction while HER mechanism for Ni foam was Volmer-Heyroovsky[62].

It is worth noting that it is not always easy to interpret the mechanism by Tafel slope. Liu and et al. studied both hydrogen and oxygen evolution capability of a water soluble copper complex. For HER, the electrocatalyst possessed a Tafel slope of 320 mV/dec. This high Tafel slope can be contributed to catalytic properties of the CuCat as well as reduction of copper species[63]. High Tafel slopes like this case indicate the complicated processes occurring in the system.

A porphyrin based porous titanium coordination polymer (TiCP-PCP) coupled with Co_{1-x}S was prepared and utilized as an electrocatalyst for oxygen evolution reaction by Wang and coworkers[64]. Employment of TiCP-PCP in the composite had significant effect on the number of active sites as well as electronic feature of Co_{1-x}S to boost OER performance in alkaline medium. It was observed that incorporation of 20% TiCP-PCP led to the highest activity with the lowest overpotential of 157 mV vs. RHE at current density of 10 mA.cm^{-2} . According to the Tafel plots, 0.2TiCP-PCP@ Co_{1-x}S possessed the smallest Tafel slope of 65 mV.dec^{-1} in comparison with other sample containing 10 (90 mV.dec^{-1}) and 30% (118 mV.dec^{-1}) which confirmed the faster kinetics of this sample for oxygen evolution.

In summary, Tafel slopes hold characteristic information about the kinetics of the reactions. Although there are distinct values for specific reaction mechanisms, the experimental conditions such as surface defects can push the obtained Tafel slope far from those specific values[59][54].

1.2.6.2 The volcano plots and exchange current density

As it is mentioned before, HER consists of two adsorption and desorption steps. A superb HER catalyst not only has a great affinity toward hydrogen adsorption (Volmer) but also can efficiently release these adsorbed hydrogen species from the surface (Heyrovsky and Tafel). For catalysts such as transition metal oxide, sulfides, carbides, phosphides and hydroxides, because of either the lower affinity for adsorbing hydrogen

or inferior efficiency in desorption of the surface hydrogen species, mostly Volmer reaction or in some cases, Heyrovsky step is the rate-determining step. Volcano plot, which relates the exchange current density of the certain metals to Gibbs free energy change of adsorption of hydrogen to the catalyst (ΔG_{H^+} , indicating the metal-to-H bond strength) provides an advantageous approach to evaluate the catalysts[57]. The Volcano plots follow the Sabatier principle [65] which is about the optimum binding energy for the reaction intermediates. Based on this principle, the optimum catalytic activity is obtained when the binding energy is neither too weak to prevent sufficient adsorption of reactants to the surface of the catalyst nor too strong to stop desorption of the products from the surface. These volcano plots are available for both acidic and basic media which are in great agreement with experimental as well as DFT studies. From these plots it can be realized that modifying the surface chemical properties of the catalysts for better H-binding energy would definitely result in enhanced HER activity[66].

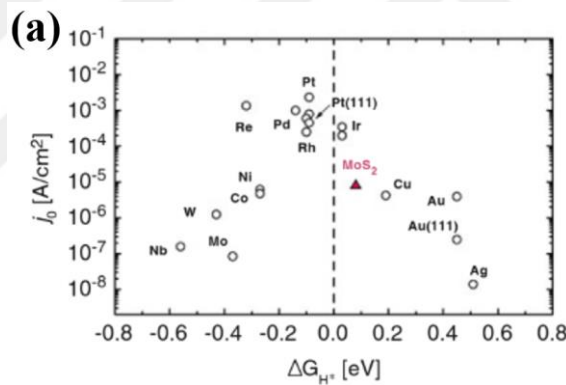


Figure 1-4– Volcano plot of exchange current density (j_0) with respect to ΔG_{H^+} values (Reprinted with permission from [57])

According to the Figure 1-4, as the Gibbs free energy change gets close to zero, the exchange current density increases. Catalysts such as Pt and Ir which show almost zero Gibbs free energy change, are considered as active catalysts for HER. Negative ΔG_{H^+} implies that atomic hydrogens are strongly adsorbed to the catalyst surface which makes hydrogen desorption step to determine the rate of the overall reaction and high overpotentials are needed to overcome this barrier. On the other hand, materials like transition metal oxides, Au and Cu possessing positive Gibbs free energy change show high Tafel slopes and make Volmer reaction as the rate-limiting step. Overall it can be concluded that the materials with high negative or positive ΔG_{H^+} are not efficient catalysts for HER [57][67].

A noteworthy point about using Volcano plots is about the impact of pH on determining the rate-limiting step of HER. Hence it is suggested to work on a 3D plot including pH as the z-axis[68]. However, these plots have already widely used to envision the capability of novel materials as electrocatalysts like MoS₂ nanoparticles for HER. This is due to the fact that mostly good HER electrocatalysts follow the rule of ΔG_{H^+} close to zero[67].

1.2.7 Electrochemical Impedance Spectroscopy

Considering an electrochemical system, it consists of mass transfer from bulk to the electrode surface, electrolyte resistance, adsorption of the electroactive species, and charge transfer at the electrode surface which all together can be served as an equivalent electrical circuit encompassing resistance, capacitance or inductor in series or parallel configuration. The most prevalent equivalent circuit for a simple electrochemical reaction is called Randles-Ershler model (Figure 1-5), which has an electrolyte resistance (R_Ω) in series with a parallel combination of a capacitor showing the effect of double-layer capacitance (C_{dl}) and a resistor for charge transfer resistance (R_{ct}). In some cases, a Warburg element (Z_W) is in series with charge transfer resistance. More details of these elements are explained later in this part. The elements of any electric equivalent circuit can be measured by electrochemical impedance spectroscopy (EIS)[69].

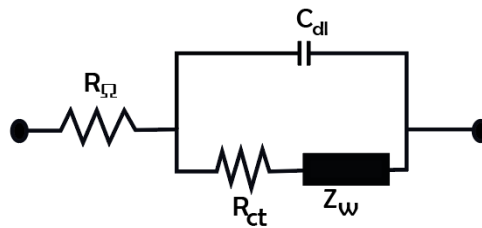


Figure 1-5- The Randles-Ershler equivalent circuit for an electrochemical cell containing electrolyte resistance (R_Ω), charge transfer resistance (R_{ct}), double-layer capacitance (C_{dl}), and Warburg element (Z_W).

When a DC voltage (Figure 1-6a) (where current is just flowing in one direction) is applied to a circuit, the resistance (R) can be calculate from Ohm's law:

$$R = \frac{V}{I} \quad (\text{Equation 1-24})$$

Where R is resistance (ohm), V is voltage (V) and I is current (A). When there is alternating current (CA) (Figure 1-6b) flowing through the system, impedance (Z) is used instead of resistance and can be calculated by:

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} \quad (\text{Equation 1-25})$$

In this equation ω represents the angular frequency of the AC voltage and Z actually measures how much the system impedes the alternating current[70].

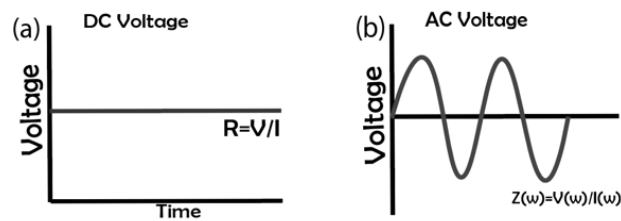


Figure 1-6- Voltage-time graph for (a) DC and (b) AC voltages.

Figure 1-7 shows a sine wave of voltage applied to a system. Due to the delay of the system in responding, the current, another sine wave, reveals a time shift as an angle, called phase angle (θ). For example, if a complete cycle (360°) of sine wave takes 1 second and the time shift is about 0.1 second, the phase angle would be 36° [71]. It is worth mentioning that a phase angle equal to zero shows the absence of time lag, meaning the resistance is technically the impedance[72].

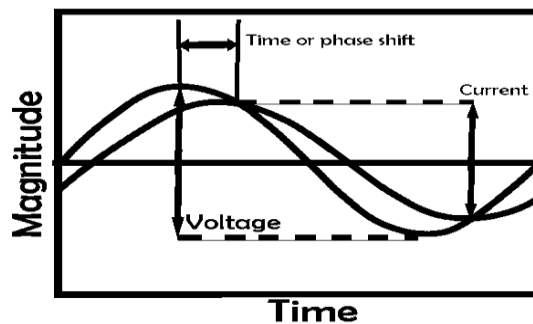


Figure 1-7- sinusoidal behavior of current and voltage as a function of time.

In impedance spectroscopy, the current is measured, as a small amplitude sinusoidal perturbation (at an angular frequency of ω) is added to a DC voltage in an electrochemical cell[73]. Changes in the impedance can be recorded in the 100 kHz to 0.001 Hz frequency range. The time response of the each component of the system

determines the frequency range[70]. The resulting impedance spectrum consists of the imaginary part (Z'') plotted against the real part (Z') of the impedance, known as “Nyquist plot” (Figure 1-8).

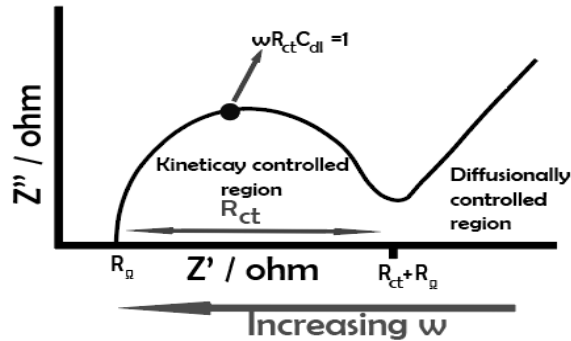


Figure 1-8- A Nyquist plot for an electrochemical system.

A Nyquist plot provides invaluable information about the electron transfer and interfacial phenomena of an electrochemical system. As it is shown in Figure 1-8, a Nyquist plot typically shows a semicircle-like trend with a straight line at the end. In this plot, each point shows the impedance at that specific frequency. Going from left side of this plot to the right, the frequency decreases. The x-intercept at high frequencies (the leftmost side of the semicircle) corresponds to the electrolyte resistance which is also known as ohmic resistance, R_Ω , and is independent of the frequency[72]. The other end of the semicircle, the lower frequency limit, reveals the sum of ohmic and charge transfer resistances ($R_\Omega + R_{ct}$). In other words, the radius of the semicircle is equal to the charge transfer resistance[72]. Recalling the Randles equivalent circuit, the charge transfer resistance and the double layer capacitor are in parallel combination. When the frequency is very low, the capacitor becomes like an open circuit and the current would only pass through the two resistors. In this case the total impedance is the sum of the individual values (Figure 1-9a). Whilst the capacitor starts showing the resistive behavior at high frequencies that at some point its impedance becomes smaller than charge transfer resistor. Reaching to the high frequency limit, the capacitor acts like a wire and the current would solely through the capacitor, not from R_{ct} . The circuit can be presented as Figure 1-9b and R_Ω is the only factor causing the impedance of the system.

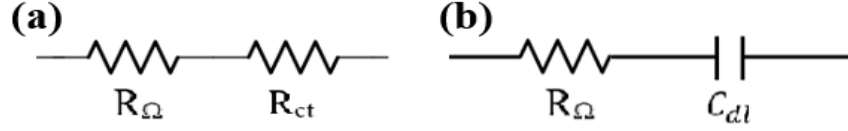


Figure 1-9– Simplified Randles equivalent circuit for an electrochemical cell at (a) low-limit and (b) high-limit frequencies. The total impedance would be equal to (a) $R_{\Omega} + R_{ct}$, and (b) R_{Ω} .

In addition to these, double layer capacitance (C_{dl}) can be calculated using the maximum point of the semicircle in the Nyquist plot as[70]:

$$\omega_{max} = \frac{1}{R_{ct}C_{dl}} \quad (\text{Equation 1-26})$$

In a system which diffusion to and from the electrode have impact on the charge transfer, another feature, known as Warburg Element is observed in the equivalent circuit. In such systems where Warburg impedance is also present in the EIS spectrum, it can be deduced that the cell is controlled by both kinetics as well as diffusional processes. Warburg Element can be identified by an oblique line with an angle about 45° in the low frequency –right side of the Nyquist plot- region[74].

Another plot that can be obtained from electrochemical impedance spectroscopy is Bode plot (Figure 1-10). Here logarithm of frequency ($\log(\omega)$) is on the x-axis where logarithm of absolute value of impedance ($|Z|$) and phase angle on the ordinates. Using the curve of $\log(|Z|)$ vs. $\log(\omega)$, two parameters of R_{Ω} and R_{ct} can be obtained. As it was mentioned earlier, $|Z|$ does not depend on the frequency at very high and very low frequencies and the highest and the lowest frequencies contribute to $\log(R_{\Omega})$ and $\log(R_{\Omega} + R_{ct})$, respectively. In the second case, the phase angle should be zero, indicating a pure resistive behavior[71].

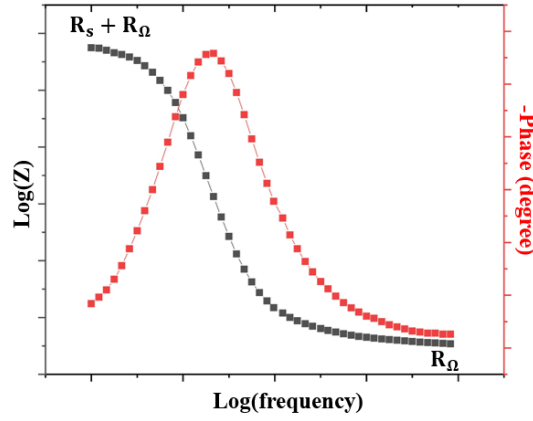


Figure 1-10- Bode plot for an electrochemical cell

The significant difference between Bode and Nyquist plots is about the frequency. In Bode plot, frequencies are explicitly shown for each measured point, while it is not plausible to distinguish the frequency of the corresponding impedance from Nyquist plot[71][75]. Furthermore, it is easier to identify small impedances coexisting with the large ones in Bode plot[71].

1.2.8 Kramers-Kronig (K-K) transforms

Performing any impedance analysis needs to be followed by the validation of the data, especially when the amplitude of the excitation is low or the system is regarded as a noisy one[76]. This validation is done using Kramers-Kronig relations. As it is shown in equations 1-27, 1-28, and 1-29, the real part of the impedance can be calculated from the imaginary part and vice versa[77].

For the real part:

$$Z_{re}(\omega) = Z_{re}(\infty) + \frac{2}{\pi} \int_0^{\infty} \frac{x Z_{im}(x) - \omega Z_{im}(\omega)}{x^2 - \omega^2} dx \quad (\text{Equation 1-27})$$

Or

$$Z_{re}(\omega) = Z_{re}(0) + \frac{2\omega}{\pi} \int_0^{\infty} \frac{(\omega/x) Z_{im}(x) - Z_{im}(\omega)}{x^2 - \omega^2} dx \quad (\text{Equation 1-28})$$

And for the imaginary part:

$$Z_{im}(\omega) = \frac{2\omega}{\pi} \int_0^{\infty} \frac{Z_{re}(x) - Z_{re}(\omega)}{x^2 - \omega^2} dx \quad (\text{Equation 1-29})$$

There are four conditions for a system to pass through K-K test:

- i) Causality: it must be only the applied perturbation that gives rise to the response of the system.
- ii) Linearity: the impedance must include only the first order response. Systems like electrodes that show nonlinearity are accompanied by a small perturbation voltage which is usually less than 10 mV.
- iii) Stability: when the perturbation is eliminated from the system, it should cease oscillating. Also no change should be observed with time.
- iv) At all values of frequency, even $\omega \rightarrow 0$ and $\omega \rightarrow \infty$, the impedance must be finite.

Overall, any impedance data needs to be confirmed by the KK transform. If the difference between the experimental and transformed data exceeds the experimental error range, the impedance data is debased[76].

Zhuang and co-workers synthesized TCPP/Cu₂O composites, using different content of 5,10,15,20-meso-tetra(4-carboxyphenyl)porphyrin (TCPP) assembled with cuprous oxide nanosheets. Both peripheries and center of the TCPP were in interaction with Cu₂O. This composite showed a photocatalytic behavior toward hydrogen production which was examined in a 5:1 solution of water and triethanolamine using a 300 W Xe lamp as the sun simulator. They observed that the composite containing 25% TCPP exhibits the best photocatalytic performance in comparison with pure Cu₂O, pure TCPP, 15%TCPP/Cu₂O and 50%TCPP/Cu₂O. One of the measurements taken to compare the photocatalytic activity of the various composites was impedance spectroscopy. As it is shown in Figure 1-11, addition of TCPP significantly influenced the electron transfer in the system as the diameter of the semicircles decreases. Furthermore 25%TCPP/Cu₂O possesses the smallest charge transfer resistance as the less amount of TCPP does not provide enough contact between TCPP and Cu₂O while excess amount of TCPP prohibit fast electron transfer by aggregating. Overall they concluded that introducing TCPP into Cu₂O enhances the catalytic activity of non-precious metal Cu₂O photocatalyst[78]. By comparing this study with our case, although there is less metal in our composite, the charge transfer resistance is much smaller than here.

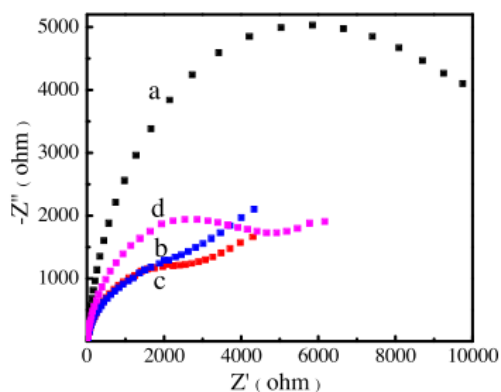


Figure 1-11- Nyquist plots for Cu₂O (a), 15%TCPP/Cu₂O (b), 25%TCPP/Cu₂O (c) and 50%TCPP/Cu₂O (d) (Reprinted with permission from [78])

In another study, (metallo)porphyrin-based imine gels were investigated for photocatalytic hydrogen evolution capability by Liao and co-workers. Therefore, free base and metallated 5,10,15,20-tetrakis(p-aminophenyl)porphyrin (MTAPP, M=H₂, Pd and SnCl₂) derivatives were reacted with 1,3,5-tris-(4-formyl-phenyl)triazine (TFPT). PdTAPP-TFPT aerogel showed a broad absorption band in the visible region through diffuse reflectance UV/Vis spectrum, i.e. when the gel is irradiated with visible light, it can absorb photons. Tauc plot was used to estimate the optical bandgap of it which is about 1.60 eV, validating the use of this gel for water splitting purposes. The electrochemical measurements were performed by using FTO coated with porphyrin-based imine gel as working electrode, Ag/AgCl as reference electrode and Pt counter electrode in a three-electrode cell configuration. They tried different deposition amounts and as it is depicted in Figure 1-12, going from 2 μ l to 4 μ l enhancement in the photocatalytic activity was observed. Also the bare FTO and H₂TAPP-TFPT do not show any significant cathodic current toward hydrogen production. Electrochemical impedance spectroscopy was utilized to compare the charge transfer resistance of the PdTAPP-TFPT samples. The sample containing larger amount of coating (4 μ l) showed smaller semicircle behavior, indicative of the faster electron transfer than 2 μ l coated sample. These results also confirm the improved HER performance of this sample in the LSV curves. Finally, PdTAPP-TFPT sample doped with Pt as co-catalyst and in the presence of sodium ascorbate as the sacrificial agent was able to produce 1.0744×10^5 μ mol/gr during 120 hr[79].

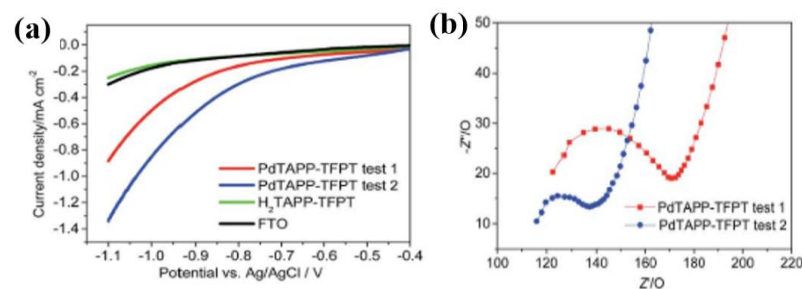


Figure 1-12- (a) LSV curves and (b) Nyquist plots of samples containing 2 and 4 μl of catalyst in neutral solution of 0.1 M KH_2PO_4 . (Reprinted with permission from [79])

Also Li and co-workers were able to synthesize naphthalimide-porphyrin (NP)/ $\text{g-C}_3\text{N}_4$ hybrids with different content of NP through impregnation method. π - π stacking is the driving force of adsorbed planar NPs on the two dimensional $\text{g-C}_3\text{N}_4$ and owing to the extension in absorption band of the $\text{g-C}_3\text{N}_4$, the hybrids were used as photocatalysts to produce hydrogen. The sample containing 2% NP showed a significant photocatalytic activity in comparison with pristine $\text{g-C}_3\text{N}_4$. This superiority was further confirmed by electrochemical impedance spectroscopy. According to the Nyquist plots in Figure 1-13, the data was fitted to Randles equivalent circuit and as the diameter of 2%NP/ $\text{g-C}_3\text{N}_4$ semicircle is smaller than the one for $\text{g-C}_3\text{N}_4$, it can be concluded that the presence of NP facilitates the electron transfer in the system, resulting in smaller charge transfer resistance (R_{ct}). In general, they were able to synthesize NP/ $\text{g-C}_3\text{N}_4$ hybrids with faster electron transfer in the system. The best photocatalytic activity was obtained when 2% NP was impregnated into $\text{g-C}_3\text{N}_4$ and it could produce 2297 $\mu\text{mol/gr.hr}$ hydrogen in triethanolamine solution with 3wt% Pt as co-catalyst[80]. It is worth mentioning that they used high content of precious metal, Pt. Also compared to the Nyquist plot of our sample, 2%NP/ g-CN possesses a larger semicircle arc.

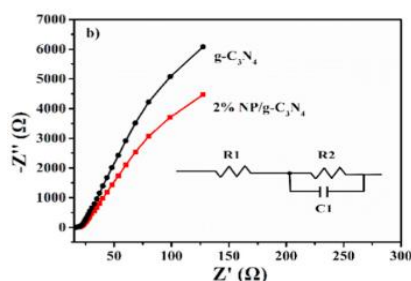


Figure 1-13- Nyquist plots for $\text{g-C}_3\text{N}_4$ and 2%NP/ $\text{g-C}_3\text{N}_4$ (Reprinted with permission from [80])

Dai[81] and et. al. reported the synthesis and electrocatalytic activity of a 3D non-interpenetrating porous metal-organic framework $[\text{Pb}_2(\text{H}_2\text{TCPP})]\cdot 4\text{DMF}\cdot \text{H}_2\text{O}$ (Pb-TCPP) (H_6TCPP = 5,10,15,20-tetra (carboxyphenyl)porphyrin). This Pb-MOF was able to show gas sorption for N_2 , H_2 , CO_2 , and Ar. The electrocatalytic activity of Pb-TCPP was examined in three different solvents (0.1 M KOH, 1.0 M KOH, and 0.2 M PBS). Although Pb-TCPP was not able to reach $10 \text{ mA}\cdot\text{cm}^{-2}$, this sample showed higher activity in basic solution with 1.70 and 1.79 V at 1.0 and 0.1 M KOH, respectively. This superiority was also confirmed in electrochemical impedance spectroscopy results. The charge transfer resistance on the surface of the catalyst was decreased to the smallest amount of 40Ω in 1.0 M KOH. As it was mentioned before, R_{ct} is reversely related to electrocatalytic performance, implying that Pb-TCPP had the best performance in 1.0 M KOH solution toward OER.

1.2.9 Faradaic efficiency

Faradaic efficiency (Λ) is the ratio of catalytic reaction rate to faradaic rate. For electrolysis this value is $\Lambda \leq 1$ while for electrochemical promotion, $\Lambda > 1$ and this is the major distinguishing factor between these two processes[82].

This parameter is also reported for HER electrocatalysts indicating how selective the catalyst is toward producing hydrogen, meaning that the higher Λ is, the electrocatalyst favors HER reaction more than other side reactions. In order to calculate this value for an HER electrocatalyst, the amount of hydrogen produced experimentally is divided by the theoretical amount. The experimental value can be obtained using gas chromatography (GC) equipment or also chronoamperometry experiment can be a helpful measurement in this regard. Overall Faradaic efficiency can be theoretically found using equation below:

$$\Lambda = \frac{nNF}{Q} \times 100\% \quad (\text{Equation 1-30})$$

where n is number of electrons transferred through the reaction ($n=2$ for HER), F is Faraday's constant, N can be calculated from chronoamperometry measurement (explained in the next part) and represents the generated H_2 during the experiment and

finally Q is the total charge crossing through the system obtained from potentiometric results.

1.2.10 Turn-over frequency

Talking about the activity of a catalyst, the number of available active sites on the catalyst. Turnover frequency is a practical criteria to evaluate catalytic activity and compare similar catalysts. This parameter can presents the intrinsic rate of a reaction derived by a catalyst and can be defined as the number of produced molecules per time per active sites of the catalyst.

$$\text{TOF} = \frac{\text{The amount of products in moles}}{\text{Number of active sites} \times \text{time}} [\text{s}^{-1}] \quad (\text{Equation 1-31})$$

In heterogeneous catalysis, determining the real number of active sites for the catalyst is complicated, reported TOF is not accurate. Whilst this is common to report TOF for homogeneous catalysis[50].

TOF can be also used in catalytic water splitting. In this case, the number of produced hydrogen (in HER) or oxygen (in OER) is considered. Mostly mass of the metal catalyst is employed to calculate number of active sites while assuming that all metal ions are participating in the reaction. Hence equation 1-31 can be further simplified to equation 1-32 for H₂ production:

$$\text{TOF} = \frac{jA_e}{2Fm} \quad (\text{Equation 1-32})$$

Where j is current density (A.cm⁻²), A_e is the electrode surface area, F is faraday's constant and m is number of moles of metal ions.

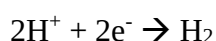
1.2.11 Faraday's law

The amount of product (N in mol) is proportional to the total charge (Q in coulomb) crossing through a system. In other words, producing 1 mole of product requires passage of 96485.4 C charge in the cell. This can be represented in the form of:

$$Q = nFN \quad (\text{Equation 1-33})$$

Where n stands for the number of electrons transferred per 1 equivalent reaction and F is Faraday's constant.

Faraday's law is widely used to calculate the required electricity for an electrolysis process (coulometry) and also the deposition amount on an electrode (electrogravimetry). This equation has a particular importance in obtaining the number of electrons participating in a redox reaction[53]. Having the redox reaction of H^+ / H_2 as:



It can be understood that producing 1 mole of H_2 , two electrons ($n=2$) are essential to drive the reaction. Hence the system needs 19.30×10^4 C to pass through.

1.2.12 Electrochemical surface area

Since catalytic reactions happen on the surface of catalysts, the active sites available on the surface play an important role in characterizing a catalyst. Hence a term called “electrochemical surface area (ECSA)” is introduced which describes the active centers on a solid electrode. The real area of a solid electrode can exceed its geometric area, even being 100 times greater. This number can also vary for different electrodes and consequently, can be used as a practical parameter to compare the activity of catalysts, making it essential to have subtle understanding of ECSA[83].

One of the methods to obtain ECSA is by measuring the electric double layer capacitance (C_{dl}). In this regard, an appropriate potential window is chosen where merely charging and discharging of double layer occurs. This potential window is placed between the hydrogen and oxygen regions. For instance, this potential range is from 0.4 V to 0.70 V vs. RHE for Pt and Pb. However, in some metals such as Ru, it is not plausible to distinguish this region as the hydrogen and oxygen regions are overlapping[84][83]. Based on double layer capacitance method, series of cyclic voltammetry are performed in the as mentioned region at different scan rates. Then the capacitive current density is plotted against the scan rate. As this current is just because of double layer charging/discharging and no faradaic current exists there, the plot shows linearity which according to the following equation, its slope is equal to double layer differential capacity:

$$i = \frac{dQ}{dt} = \left(\frac{dQ}{dE}\right) \cdot \left(\frac{dE}{dt}\right) = C \cdot v \quad (\text{Equation 1-34})$$

The slope can be used to compare activity of same catalysts, meaning that the higher the slope is, the more active centers are available for catalytic reaction. Ma and co-workers[84] reported the electrocatalytic activity of CoTMPyP/ERGO toward hydrogen production. After preparing CoTMPyP functionalized graphene oxide (CoTMPyP/GO) by mixing GO and CoTMPyP with 3 to 1 ratio in water at 50 C for 12 hr, a homogenous ink was achieved by dispersing 2 mg of this sample in 1 ml of water. Then known amount of the ink was drop casted on a glassy carbon electrode and electrochemical reduction of CoTMPyP/GO was conducted through 30 cyclic voltammograms in PBS solution in 0 to -1.5 V potential window. For the sake of comparison, the same procedure was done for GO. The electrochemical surface area was measured for the samples by measuring the electric double layer capacitance (C_{dl}) in 0.1 – 0.2 V vs. RHE potential range. After plotting capacitive current density versus scan rates, they observed that CoTMPyP/ERGO significantly increased the active surface area, having higher capacitance of 23.5 mF.cm⁻² than 10 mF.cm⁻² of ERGO electrode. Finally it was shown that CoTMPyP/ERGO is an active and stable electrocatalyst in alkaline medium toward hydrogen production.

Meng and coworkers[85] studied the electrocatalytic activity of a bimetallic porphyrin MOF supported on reduced graphene oxide toward oxygen evolution in alkaline solution. This 2D electrocatalyst was fabricated through loading Co–CuTCPP nanosheets onto graphene oxide by a hydrothermal method with three different ratios of GO to porphyrin (0.5:1, 1:1 and 2:1). It was shown that Co–CuTCPP/rGO-10 (1:1) had the highest activity by reaching to the current density of 10 mA.cm⁻² at overpotential of 396 mV. Measuring double layer capacitance (C_{dl}) was employed to compare the catalytic activity as well as active sites of these electrocatalysts. Cyclic voltammetry experiments were performed from 0.5 to 1.4 V at various scan rates of 20 to 60 mV.s⁻¹. The significantly increased slope of Co–CuTCPP/rGO-10 (2.54 mF.cm⁻²) in comparison with pure Co–CuTCPP (0.93 mF.cm⁻²) highlighted the impact of better dispersion of Co–CuTCPP in enhancing the number of available catalytic active sites. This improved behavior is attributed to the synergetic effect of co-existence of Cu and Co metals with rGO in the composite.

ECSA is then calculated by:

$$ECSA = \frac{C_{dl}}{C_{ref}} \quad (\text{Equation 1-35})$$

Where C_{ref} stands for reference value of capacity per area which is actually the major reason for errors in reporting ECSA. Since differential capacity highly depends on structure of the surface, applied potential, electrolyte concentration and composition, and even slight experimental changes, reported C_{ref} can differ.

Nitrogen-enriched porous carbon materials with copper/copper oxide synthesized from copper porphyrin-based conjugated mesoporous polymer (Cu-CMP) were utilized as bifunctional electrocatalysts for both HER and OER by Cui and co-worker. Cu-CMP samples were heated at different temperatures of 500, 600, 700, 800, 850 and 900 °C for 2 hr. Then the sample was dispersed in ethanol and Nafion mixture. Using drop-casting method, glassy carbon electrode was coated with as-prepared ink and employed as the working electrode in a three-electrode cell for electrochemical measurements. In order to calculate ECSA, series of cyclic voltammeteries were performed in the range of 1.01 – 1.11 V vs. RHE in 1.0 M KOH for all the samples. Cu-CMP850 exhibited the highest double layer capacitance of 11.1 mF and by having 40 $\mu\text{F} \cdot \text{cm}^{-2}$ as the reference value for Cu, ECSA was calculated to be 277 cm^2 (185 time larger than not-thermally treated sample) which could contribute to superior electrocatalytic activity of this sample in comparison with others. Overall, they showed that pyrolysis of Cu-CMP sample at 850 °C would result in having an active electrocatalyst capable of producing both hydrogen and oxygen in 1.0 M KOH electrolyte at room temperature[61].

1.3 Aim of study

This study examines the application of a cucurbit[6]uril-porphyrin (TPP-CB[6]) conjugated network with nickel salt as an efficient electrocatalyst for water splitting. In this work, the effect of various nickel concentration on electrochemical behavior of the composite for both hydrogen and oxygen evolution reactions was investigated. Basically the TPP-CB[6] network was first used with titanium dioxide and studied in three different acidic, neutral, and basic electrolytes. After optimizing the experimental conditions, nickel was added to the composite to enhance the catalytic activity. Meanwhile titanium dioxide was eliminated and further studies were focused on evaluating the impact of different weight percentages of Ni in the catalyst. Oxygen

evolution experiments were also performed using these x%Ni@TPP-CB[6] composites. All aforementioned parameters were employed to indicate the optimum sample for HER and OER. Then this sample was thoroughly characterized using scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and X-ray diffraction and X-ray photoelectron spectroscopy (XPS).

To the best of our knowledge, this is the first report on using cucurbit[6]uril-porphyrin conjugated network with a non-precious metal as an electrocatalyst for both hydrogen and oxygen production. The sluggish kinetics of oxidative oxygen production reaction has made it challenging to develop efficient electrocatalysts for water splitting process. Here the presence of Ni would facilitate electron transfer in the system and consequently improving the catalytic activity toward both from HER and OER. Special 3d electronic distribution has given Ni metal the edge over other materials to be employed in catalysis and using its salt in the composite can decrease the cost while enhancing the catalytic activity.

Chapter 2

Experimental and instrumentation

2.1 Experimental setup

All electrochemical measurements were performed using a CHI608E potentiostat at room temperature with a conventional three-electrode cell configuration with silver/silver chloride (Ag/AgCl, 3.5 M KCl) and spiral Pt wire as the reference (RE) and counter electrodes (CE), respectively. Fluorine-doped tin oxide glass (FTO) was coated with the known amount of the catalyst and was employed as the working electrode (WE). Prior to each experiment, system was deaerated with argon gas for 30 minutes. FTO surfaces were cleaned by washing them with water and soap, followed by ultrasonication in deionized water and isopropanol each for 10 min. Then they were activated in furnace at 450°C for 45 minutes.

2.2 Preparation of working electrode

Three sets of composites were prepared as following: first one was prepared by grinding titanium dioxide and TPP-CB6 with 2 to 1 ratio and suspending the prepared fine powder in water, ethanol and Nafion (5% in water). In the second ink, nickel acetate tetrahydrate was also ground with TiO_2 and TPP-CB6. The third ink was constituted of TPP-CB6 and $\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ in the same solvent mixture. All inks were magnetically stirred overnight to obtain a uniform ink for coating FTO.

2.3 Instrumentation

TPP-CB6, and TPP-CB6@12%Ni were characterized using available characterization devices before any electrochemical measurements. After performing electrochemical measurements and choosing the optimum sample, it was then thoroughly characterized using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR). It should be noticed that the second set of characterizations were performed on FTO surface.

2.3.1 Scanning Electron Microscopy (SEM)

In order to study topography and composition of samples, FEI Quanta 200 FEG ESEM instrument was utilized which also provided Energy-dispersive X-ray spectroscopy (EDAX) for examining the composition.

2.3.2 X-ray photoelectron spectroscopy (XPS)

Here Thermo Scientific K-Alpha X-Ray Photoelectron Spectrometer device was used for the surface chemistry analysis. This device is equipped with an AlK α monochromator source operating at 400 mm spot size and $h\nu=14.866$ eV which is accompanied with a flood gun as charge neutralization tool with 200 eV and 30 eV for survey and individual scans, respectively. C1s spectrum of the carbon support at 284.6 eV was used as the reference binding energies for all the measurements.

2.3.3 X-ray diffraction (XRD)

The crystalline structure of samples were analyzed using XPert Pro Mutipurpose X-Ray Diffractometer (MPD). In this regard, CuK α X-Ray Radiation ($\lambda=1.5418$ Å) with 2θ diffraction angle of 4-80°, step size of 0.03 and time per step of 500 seconds.

2.3.4 Fourier transform infrared spectroscopy (FT-IR)

In order to characterize the functional groups in the structure Bruker Alpha Platinum-ATR spectrometer was utilized to record Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR FT-IR) in transmission mode for the wavenumber range of 400 – 4000 cm^{-1} .

2.3.5 Electrochemical measurements

As it is mentioned earlier, CHI608E potentiostat with a conventional three-electrode cell configuration was used for all electrochemical measurements. Linear sweep voltammetry (LSV) experiments were conducted in the potential window of 0 to -1 V vs. RHE for HER and 0 to 2.4 V vs. RHE for OER measurements at scan rate of 10 mV.s^{-1} in 0.1 M KOH solution as the electrolyte. Electrochemical impedance spectroscopy (EIS) measurements were performed at potentials close to onset potential and the results were validated using KK transform[76]. For chronopotentiometry experiment, current densities were adjusted at -1 and 1 mA.cm^{-2} and the potential was measured with respect to Ag/AgCl reference electrode. Details of cyclic voltammetry as well as chronoamperometry experiments are presented in the next chapters.

Chapter 3

Results and discussion

3.1 Introduction

This section starts with a short description of synthesis and characterization of cucurbit[6]uril-porphyrin conjugate. Then titanium dioxide was added to the network and its electrochemical behavior toward HER was examined in three different electrolytes and after choosing the best electrolyte solution in terms of catalytic activity and durability, a series of electrochemical measurements were conducted and the electrode was thoroughly characterized by scanning electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy. In the next step, the effect of insertion of nickel salt (in presence and absence of TiO_2) was examined. After performing the electrochemical measurements, it was concluded that elimination of TiO_2 resulted in better electrocatalytic behavior. Afterwards, various concentration of Ni was added to the composite and by employing the electrochemical measurements, the optimum composition was chosen for both HER and OER. Finally, the structure and morphology of the optimal sample were characterized.

3.2 Synthesis and characterization

3.2.1 Synthesis of CB6-porphyrin network

A CB[6]-porphyrin supramolecular assembly has been synthesized by our group's member, Aisan Khaligh, through copper-catalyzed azide-alkyne cycloaddition reaction (Cu-AAC) between properly functionalized porphyrin and cucurbituril monomers as depicted in Figure 3-1.

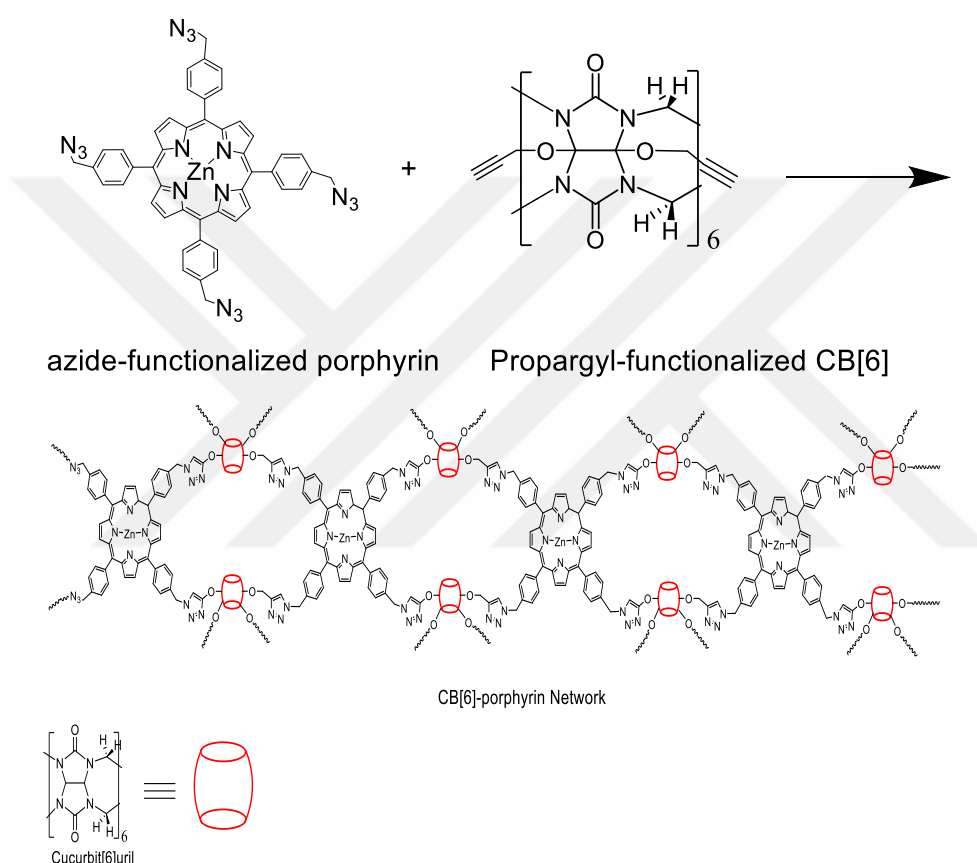


Figure 3-1- Synthesis of CB[6]-porphyrin supramolecular assembly.

The completion of this click reaction was checked by comparing the FT-IR spectra of the initial reaction mixture and the reaction mixture at different time intervals. Figure 3-2 shows the FT-IR spectra of the initial reaction mixture containing azide-functionalized porphyrin and alkyne-functionalized CB[6] monomers and the reaction mixture after 4 days reaction which contains target CB[6]-porphyrin assembly. Therein, decrease in the intensity of the azide and alkyne signals at 2095 cm^{-1} and 3258 cm^{-1} , respectively, as well as the presence of carbonyl signal at 1735 cm^{-1} in the FT-IR spectrum of the final reaction mixture compared to the initial reaction mixture confirmed the success of Cu-AAC reaction.

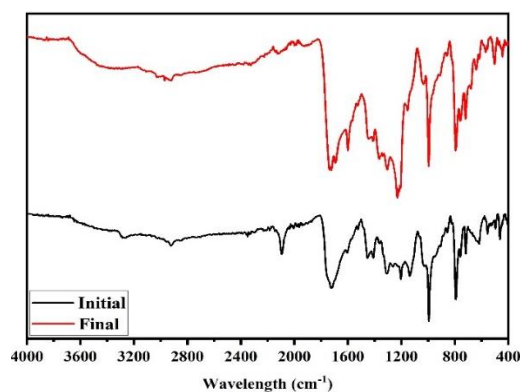


Figure 3-2- FT-IR spectrum comparing the initial and final state of the reaction mixture.

3.2.2 Characterization of CB6-porphyrin network

The SEM images of the CB[6]-porphyrin assembly showed a porous structure (Figure 3-3). The elemental composition of CB[6]-porphyrin was studied by EDX-SEM and the corresponding EDX spectrum was displayed in Figure 3-3(b). The EDX analysis showed the presence of 65.3% C, 11.95% N, 21.47% O and 1.28% Zn (atomic % by element).

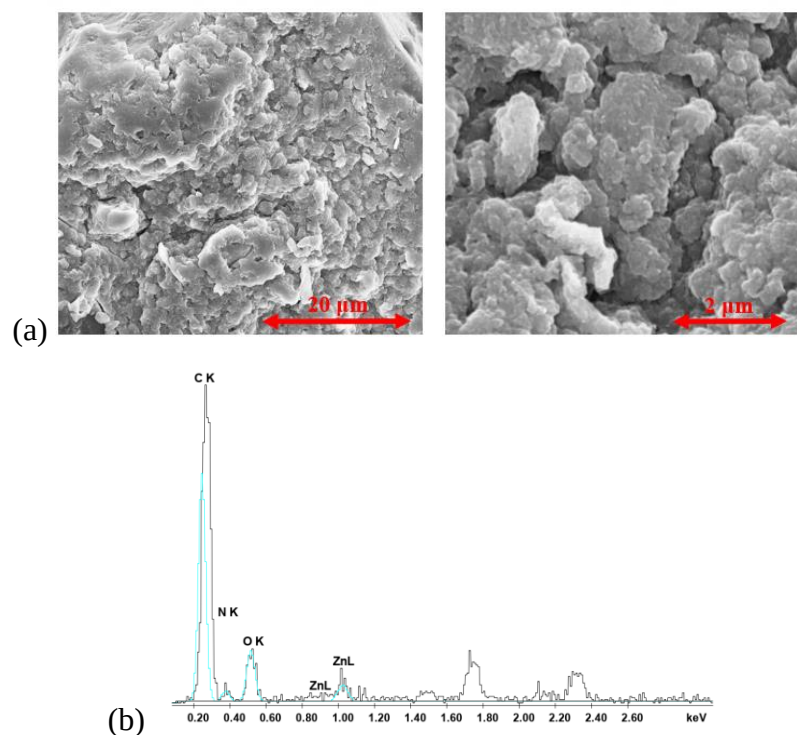


Figure 3-3- (a) SEM image and (b) EDX/SEM spectrum of CB[6]-porphyrin assembly.

3.2.3 CB6-porphyrin titanium dioxide composite

The CB6-porphyrin titanium dioxide nanocomposite was prepared by mechanochemical addition of TiO_2 to CB6-porphyrin network. According to the previous reports, this nanocomposite was prepared by grinding CB6-TPP and TiO_2 together with 2:1 ratio[86][87]. Water and ethanol as solvents and Nafion (5 wt%) as binder were added to the powder according to Table 3-1. To get a homogeneous ink, the mixture was magnetically stirred overnight.

Table 3-1- Composition of TiO_2 @TPP-CB[6] nanocomposite

Composite	TPP-CB6 (mg)	TiO_2 (mg)	H_2O (μl)	Ethanol (μl)	Nafion (μl)
TiO_2 @TPP-CB[6]	4	8	250	50	10

3.2.4 Characterization of TiO_2 @TPP-CB[6] nanocomposite

The nanocomposite was drop casted on fluorine doped tin oxide (FTO) as substrate. The morphological studies were performed using scanning electron microscopy with applying appropriate beam voltage and spot size. Figure 3-4 shows SEM images of the modified FTO. Before imaging, the samples were completely dried at room temperature.

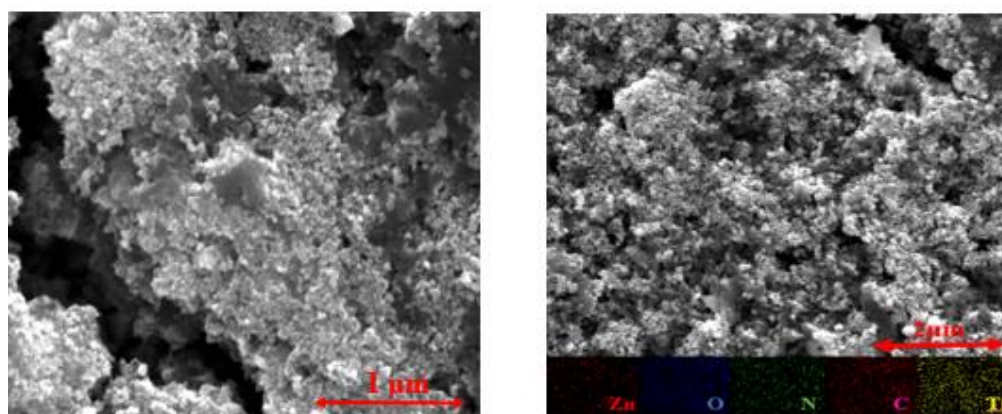


Figure 3-4- SEM images of TiO_2 @TPP-CB[6] coated on FTO and dried at RT.

X-ray photoelectron microscopy of TiO_2 @CB6-TPP is depicted in Figure 3-5. In N 1s spectrum, peak at about 397.64 eV is attributed to Zn-N binding in the center of the porphyrin which Zn^{2+} peaks are presented at 1032.75 eV (Zn 2p_{3/2}) and 1044.82 eV

(Zn 2p_{1/2}) in Zn 2p spectrum. The peaks for Ti⁴⁺2p and Ti²⁺2p can be observed in Ti2p spectrum positioned at 457, 460 and 465 eV, respectively.

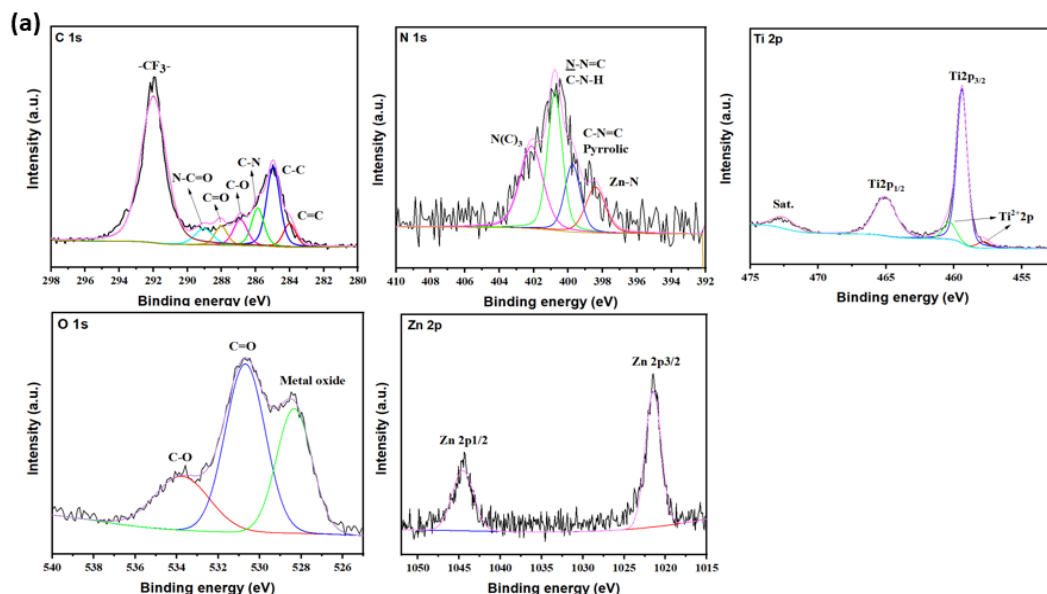


Figure 3-5- XPS spectra for TiO₂@TPP-CB[6] coated on FTO before performing electrochemical experiments.

XRD measurement was also conducted to study the crystal structure of the nanocomposite. The peak at almost 10° represents TPP-CB[6] in the composite. For preparing catalyst modified-FTO, Nafion (5 wt%) was also added on the surface of FTO. This has led to appearance of a peak at 17°.

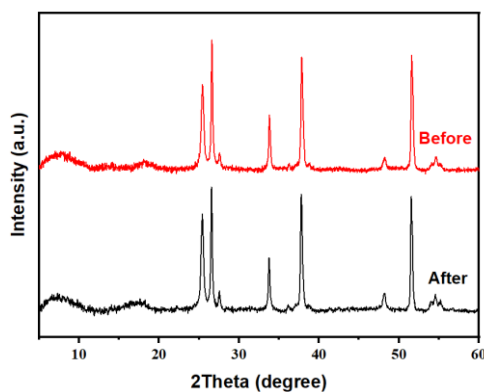


Figure 3-6- XRD pattern for TiO₂@TPP-CB[6] coated on FTO before and after electrochemical measurements in alkaline (KOH, 0.1 M) electrolyte.

3.2.5 Stability of TiO₂@TPP-CB[6] in alkaline solution

The durability of the modified FTO was examined after 3000 s of chronoamperometry experiment by conducting SEM, XRD and XPS analysis. According to the results, the sample was thoroughly stable.

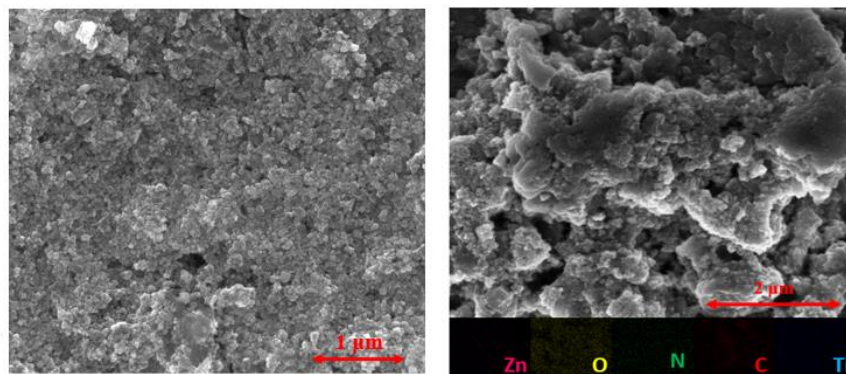


Figure 3-7- SEM images of TiO₂@TPP-CB[6] composite after electrochemical measurements performed in KOH (0.1 M).

Comparing the SEM images of the TiO₂@TPP-CB[6], before and after CA experiment (Figure 3-7), no significant change can be observed. Also elemental mapping for C, N, O, Zn, and Ti follow the same trend.

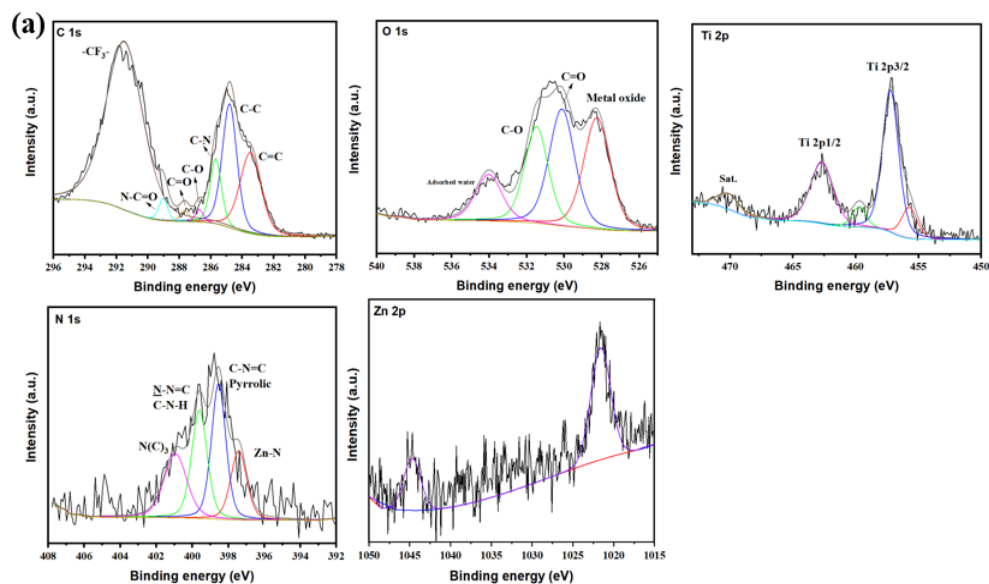


Figure 3-8- XPS spectra for TiO₂@TPP-CB[6] coated on FTO after performing electrochemical experiments in alkaline (KOH, 0.1 M) electrolyte

XPS spectra for the elemental states demonstrated comparable results (Figure 3-8). The presence of peak at 1022 and 1045 eV in Zn 2p spectrum and 397.5 eV in N 1s spectrum for Zn-N bonding proves the presence of Zn in the porphyrin center after experiment. Two extra peaks at 293.0 and 296 eV are appeared in C1s spectrum which are contributed to the 2F and 3F bound to carbon from FTO substrate. No change was presented in the spectra of the other elements.

3.2.6 x%Ni@TPP-CB6 composite

The different percentage of Ni was utilized to prepare Ni@TPP-CB6 composites. As presented in Table 3-1, nickel acetate tetrahydrate was ground with TPP-CB6. Ink was prepared as before by insertion of water, ethanol and Nafion followed by overnight stirring. FTO surface was coated with known amount of the ink and dried at RT overnight.

Table 3-2- Composition of x%Ni@TPP-CB6 inks

Composite	Nickel acetate tetrahydrate (mg)	TPP-CB[6] (mg)	H ₂ O (μl)	Ethanol (μl)	Nafion (μl)
6%Ni@TPP-CB6	1	4	250	50	10
12%Ni@TPP-CB6	2	4	250	50	10
23%Ni@TPP-CB6	4	4	250	50	10
47%Ni@TPP-CB6	8	4	250	50	10

3.2.7 12%Ni@TPP-CB[6] composite as optimum sample

3.2.7.1 Morphological studies

The morphology of the samples were analyzed using SEM (Figure 3-9). By comparing the images for before and after CA experiments, it can be understood that the structure of 12%Ni@TPP-CB6 did not collapse after both HER and OER experiments. Elemental mapping results demonstrate the consistency in elemental distribution.

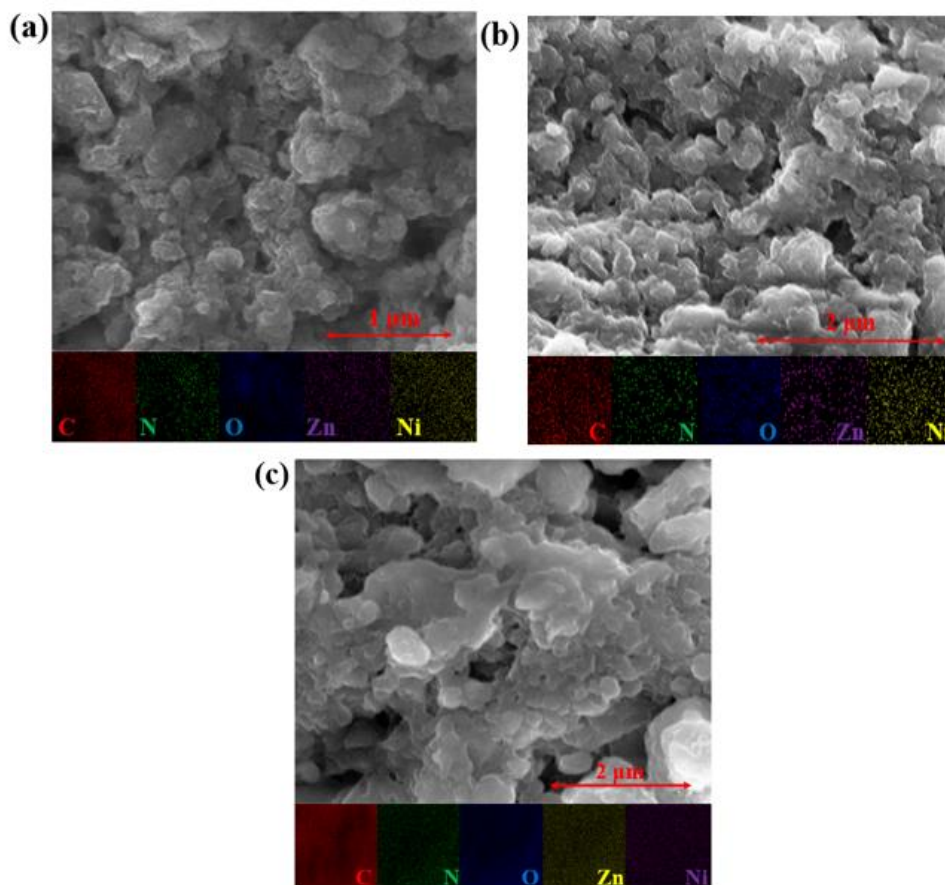


Figure 3-9- SEM images and elemental mapping of 12%Ni@TPP-CB6 (a) before, after (b) HER and (c) OER experiments.

Energy dispersive X-ray spectroscopy helped to have a better understanding of atomic percentage of different elements in the composite. After coating the activated FTO with corresponding ink and drying at RT, EDX results reveals about 5.6% and 1.2% of Ni and Zn presented in the structure. The similar values are achieved after performing HER and OER experiments which highlights the stability of our electrocatalyst.

Also SEM was employed to observe the morphology of the 12%Ni@TPP-CB[6] composite after chronopotentiometry switching between HER and OER. As it is shown in Figure 3-10, the morphology of this electrocatalyst did not collapsed and exhibited the similar structure. In addition to this, elemental mapping provides a general view of distribution of elements which alongside quantifying almost 5% for Ni and 1.2% for Zn (atomic percentages) elements in the structure, unchanged morphology as well as elemental composition of our x%Ni@TPP-CB[6] catalyst is justified.

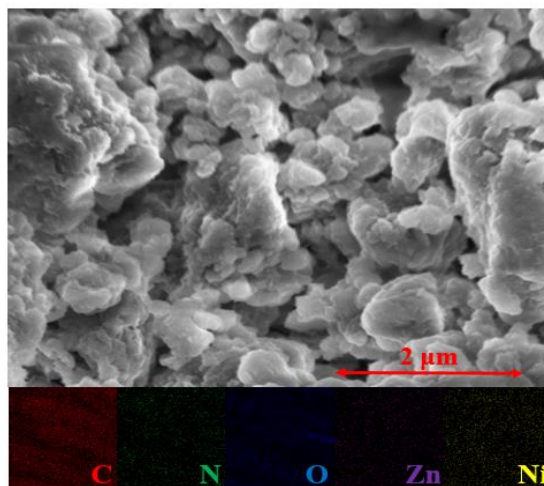


Figure 3-10- SEM image and elemental mapping of the 12%Ni@TPP-CB[6] composite after chronopotentiometry for 6000 s.

3.2.7.2 X-ray photoelectron spectroscopy (XPS)

Elemental valence states of the catalyst were studied using XPS. Figure 3-11(a) shows the XPS spectra for as prepared 12%Ni@TPP-CB6 composite on FTO. According to Ni 2p spectrum, peaks at 853.7 and 855.12 eV (Ni2p_{3/2}) as well as 871.5 and 873.6 eV (Ni2p_{1/2}) represent presence of Ni²⁺ in the composite. After HER, the XPS spectrum of Ni have the same peaks at the comparable binding energies. Decrease in the intensity of the satellite peaks of Ni can be contributed to the formation of Ni(I) under H₂ atmosphere.

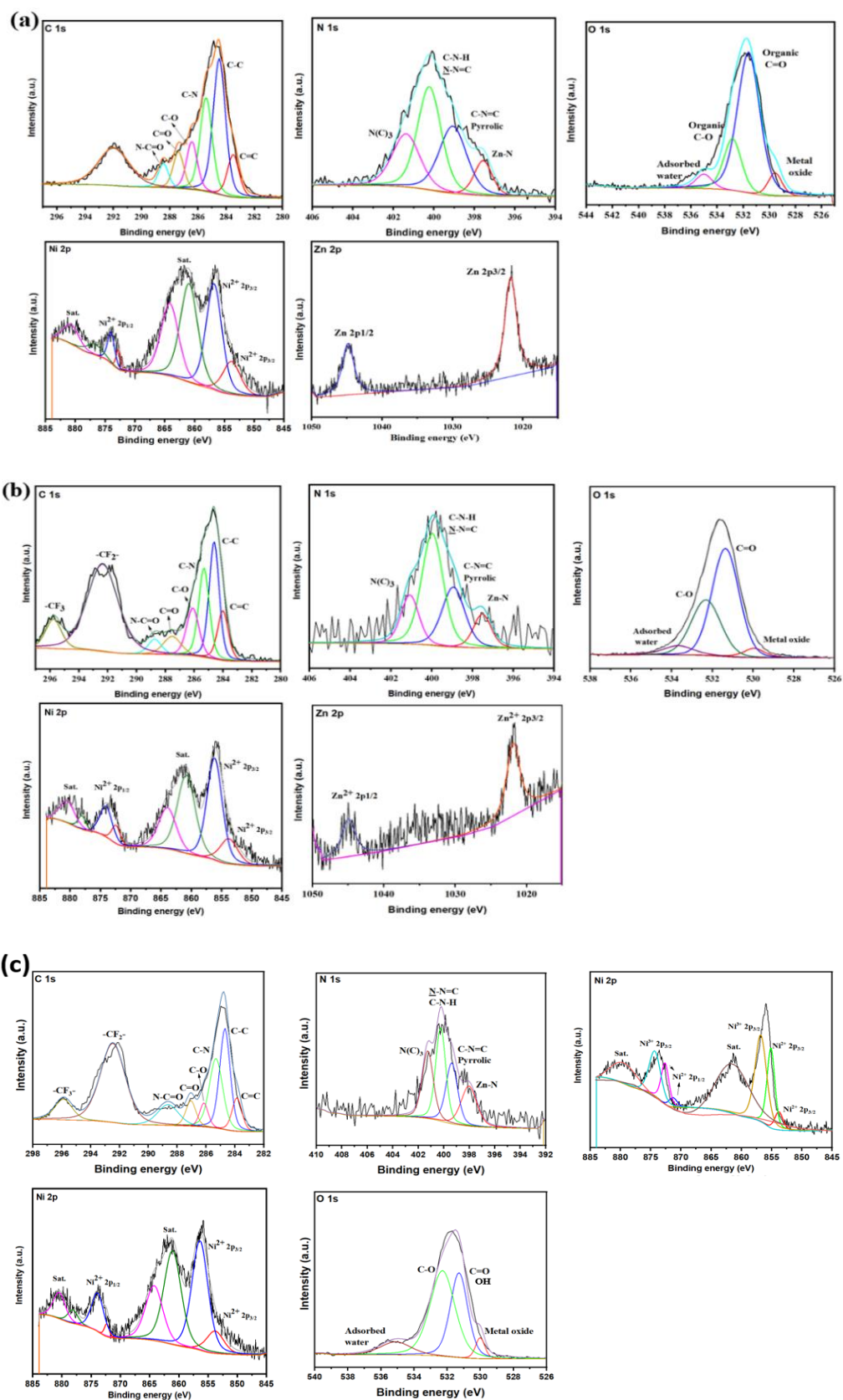


Figure 3-11- XPS data of 12%Ni@TPP-CB[6] (a) before, after (b) HER and (c) OER.

Identical peaks position in Zn2p spectrum as well as repeated peak at 398.5 eV in N1s spectrum after CA experiment justify the unchanged behavior of Zn in the center of TPP-CB[6]. No significant alteration was also observed in other elements indicating the stability of 12%@TPP-CB6 composite. Also XPS spectra obtained after OER (Figure 3-11c) exhibit retained chemical compositions as before electrochemical measurements. The binding energies of Ni 2p_{3/2} at 856.8 eV, and Ni 2p_{1/2} at 871.3 eV with satellite at 874.4 eV with the binding energy of O 1s (at 531.5 eV) reveal the probable formation of Ni³⁺ after OER which with Ni²⁺ are as the redox couple formed during oxidation.

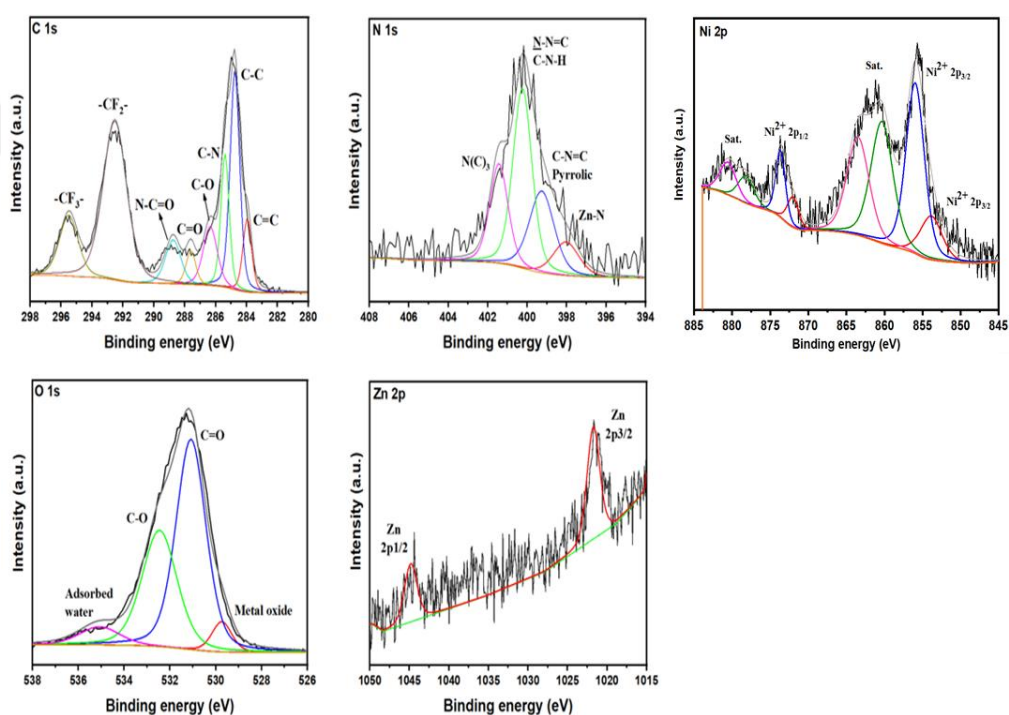


Figure 3-12- XPS data of 12% Ni@TPP-CB[6] after switching current between HER and OER.

The chemical composition of the electrocatalyst was also examined after chronopotentiometry experiment. As shown in Figure 3-12, the peak positions and types did not undergo any significant alteration which highlights the stability of 12%Ni@TPP-CB[6] employed as a bifunctional electrocatalyst.

3.2.7.3 X-ray diffraction spectroscopy (XRD)

The crystal structure of sample was also studied using XRD analysis. According to Figure 3-13, the first peak is attributed to TPP in the composite. Some peaks of Ni (51° and 61.8°) unfortunately overlapped with peaks from FTO. The small peak at 30° is related to acetates from nickel acetate tetrahydrate which is disappeared after HER and OER experiments. The analogous XRD patterns after HER and OER experiments also signify the stability of our composite.

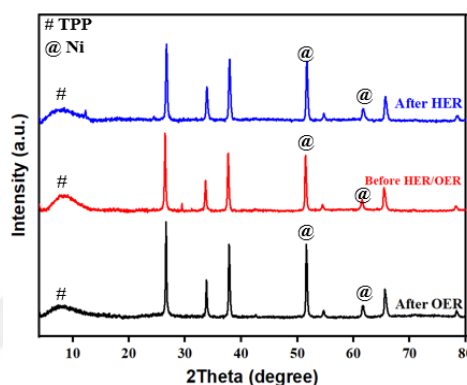


Figure 3-13 - Powder XRD spectra of 12%Ni@TPP-CB[6] comparing the structure before and after HER and OER experiments.

In order to examine the bifunctional durability of this catalyst after chronopotentiometry experiment, XRD analysis was performed after drying the sample completely. Comparing with the XRD spectrum obtained before any electrochemical experiments, comparable result is observed here as well (Figure 3-14).

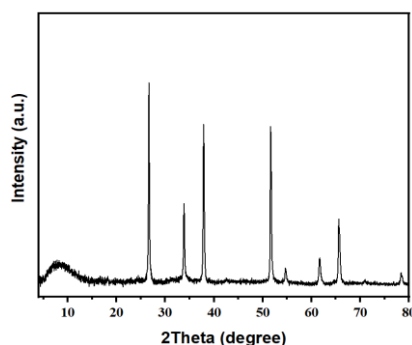


Figure 3-14 - XRD spectrum for 12%Ni@TPP-CB[6] electrocatalyst after chronopotentiometry for 6000 s in 0.1 M KOH.

3.3 Electrochemical analysis

Electrochemical measurements were conducted using a CHI670 potentiostat with a conventional three-electrode cell configuration at room temperature. In this regard, Silver/Silver chloride (Ag/AgCl, in saturated KCl) and Pt spiral wire were used as reference and counter electrode, respectively. Fluorine-doped tin oxide coated with catalyst was the working electrode in the system. First FTOs were thoroughly cleaned with soap and water. After sonication in deionized water and isopropanol for ten minutes each, the surface was activated by heating in the furnace at 450 for two hours. The catalyst was coated by drop casting method on 1×1 cm² part of FTO, dried in air overnight. Electrolytes were deaerated for half an hour prior to each experiment with Argon to remove any dissolved gases. All potentials are reported versus reversible hydrogen electrode (RHE) using equation:

$$E \text{ (vs. RHE)} = E_{(\text{Ag/AgCl/KCl (sat.)})} + 0.059\text{pH} + E_{(\text{Ag/AgCl/KCl (sat.)})}^0 \quad (\text{Equation 3-1})$$

Where E is the potential of the electrode with respect to RHE, $E_{(\text{Ag/AgCl/KCl (sat.)})}$ is the potential measured by the potentiostat, and $E_{(\text{Ag/AgCl/KCl (sat.)})}^0$ is the standard potential (0.197 V). All LSV measurements were performed at 10 mV/s with no iR compensation.

3.3.1 TiO₂@TPP-CB[6] electrocatalytic behavior

The electrocatalytic behavior of TiO₂@TPP-CB[6] nanocomposite was firstly studied by performing linear sweep voltammetry (LSV) in three different basic (0.1 M KOH), acidic (0.25 M H₂SO₄) and neutral (PBS, pH 7) electrolytes and results are shown in Figure 3-15(a).

According to LSV figures and electrochemical parameters presented in Table 3-3, the sample possessed the best catalytic behavior in acidic medium. According to the LSV curve, sample was able to reach -1 mA.cm⁻² upon applying only -493 mV vs. RHE in acidic solution, while this parameter was much more negative for sample in alkaline medium and the composite was not able to achieve this current density in neutral electrolyte. Tafel plots can provide insight into kinetics of the system. By plotting corresponding Tafel plots (Figure 3-15(b)) for the composite, it can be seen that acidic

electrolyte leads to the faster kinetics. Despite the better electrochemical behavior of the composite in the acidic electrolyte, the durability was a crucial factor. The coating was peeling off from the electrode surface after the second run. All in all, due to the slow kinetics in neutral medium and instability caused by acidic environment, the experiments were continued in alkaline electrolyte.

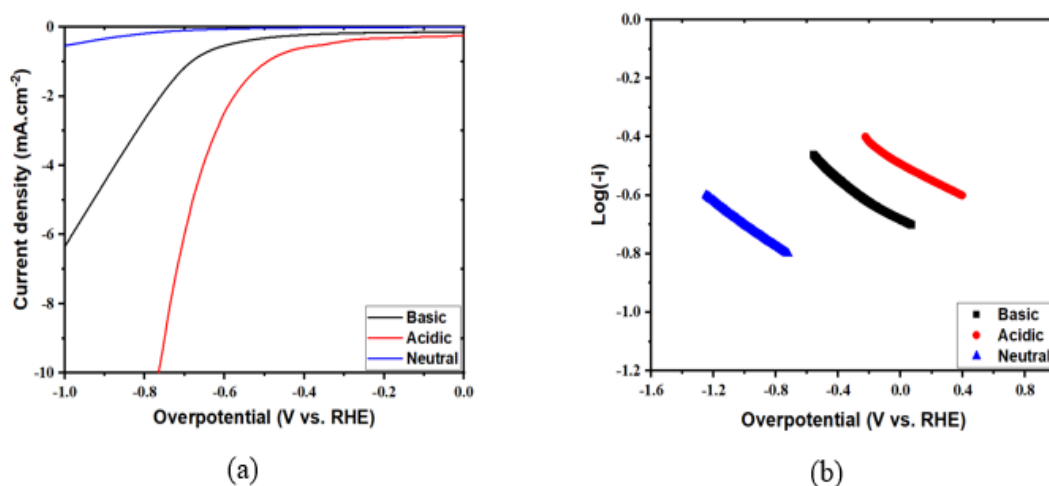


Figure 3-15- (a) LSV curves and (b) Tafel plots for TiO₂@TPP-CB[6] in three different basic (0.1 M, KOH, pH=13), acidic (0.25 M, H₂SO₄, pH=1) and neutral (PBS, pH=7) electrolytes

Table 3-3– Electrochemical parameters of TiO₂@TPP-CB[6]

Electrolyte	Onset Potential (mV)	$\eta_{-1 \text{ mA.cm}^{-2}}$ (mV)	Tafel slope (V)	j_0 (mA.cm ⁻²)
Neutral	-800	-	0.39	0.08
Acidic	-380	-493	0.31	0.33
Basic	-530	-683	0.38	0.20

3.3.2 TiO₂@TPP-CB[6] electrocatalytic behavior in alkaline electrolyte

Porphyrin structures have shown strong absorption in visible region which have led to their vast application as photosensitizers in photocatalysts for HER. Here also after preparing the catalyst coated FTO, the electrochemical experiments initiated with linear sweep voltammetry both in dark and light conditions using a 300W xenon arc lamp (with wavelength of 200 – 2000 nm). As shown in Figure 3-16, light irradiation slightly

shifted the onset of reduction reaction to a less negative value and there was a meager increase in current density. In order to have a better understanding of illumination effect, chronoamperometry experiment was performed under chopped light situation. In this regard, a potential value close to onset potential was chosen for chronoamperometry experiment during which light was switched on and off every 200 seconds. It can be clearly seen that the current density rose upon irradiation with light while it showed reverse behavior when the light was turned off. However, the current change was not sufficient enough and consequently it could be concluded that light did not have paramount impact on catalytic activity. This behavior was also reported in previous porphyrin based catalysts for water splitting[27].

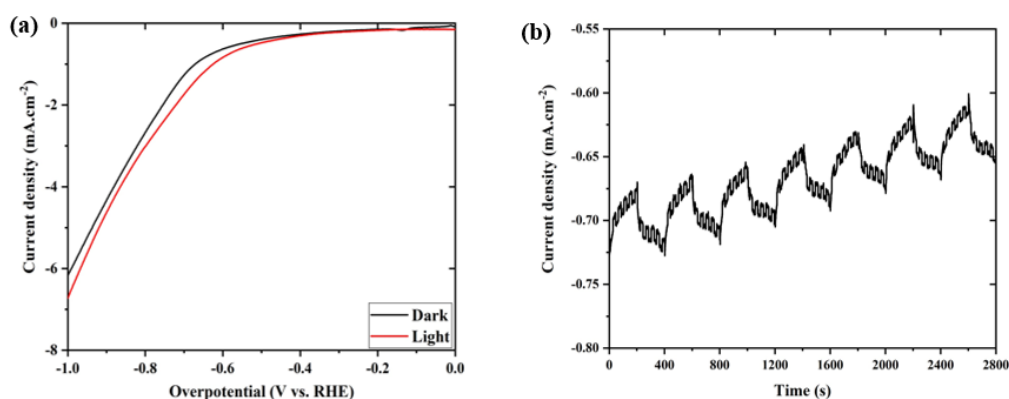


Figure 3-16-(a) Polarization curves recorded in light and dark condition, and (b) chronoamperometry experiment under chopped light illumination in 0.1 M KOH solution (pH=13).

Hence further measurements were carried on in daylight. According to the LSV curves in Figure 3-15(a), TiO₂@TPP-CB[6] had an onset potential of -0.53 V vs. RHE as an electrocatalyst in alkaline medium. As another crucial factor for catalysts, stability was examined performing chronoamperometry experiment at -0.4 V vs. RHE for 6000 s. As it is shown in Figure 3-17(a), the current response was almost stable and the unchanged onset potential and electrocatalytic behavior of the sample after CA experiment (shown in inset) proved the durability of this composite.

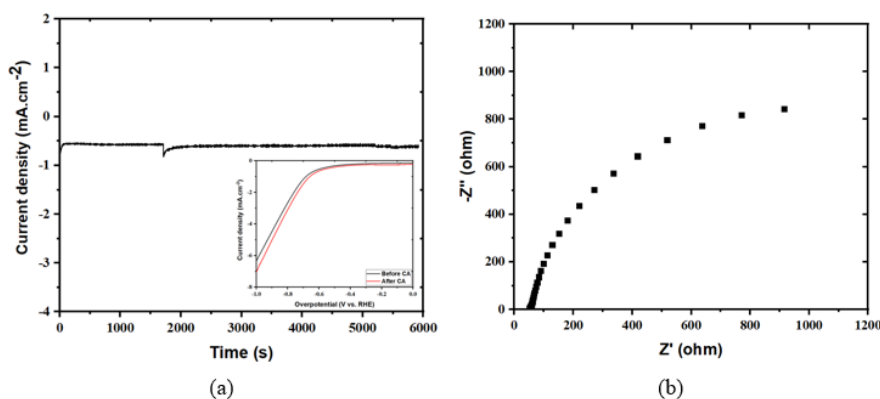


Figure 3-17-(a) Chronoamperometry experiment, and (b) Nyquist plot for $\text{TiO}_2@\text{TPP-CB}[6]$ composite both performed at -0.4 V vs. RHE in 0.1 M KOH ($\text{pH}=13$).

Similar to the previous EIS measurement, Nyquist plot was also obtained at -0.4 V vs. RHE in the frequency range of 1 Hz to 100 kHz (Figure 3-17(b)). As it is presented in Table 3-3, alkaline medium would result in slower kinetics with R_{ct} value of $1.73\text{ k}\Omega$. Overall in alkaline medium, there are three critical factors affecting the activity of a catalyst including energy required for water dissociation, hydrogen adsorption (H_{ad}) while hindering hydroxyl ion (OH^-) adsorption which is known as the poisoning agent for active sites. However, it is only energy demand for H_{ad} to the catalytic sites that dictates the activity trend of the catalyst. Hence developing efficient electrocatalyst to overcome this energy barrier in alkaline solution has become a critical research area[66].

In these experiments neither sacrificial agent nor co-catalyst was employed for HER experiments and only the porphyrin assembly was accompanied with TiO_2 . In the next section, nickel salt would be added to the composite and electrochemical behavior of the new system would be studied in details.

3.3.3 Addition of Ni

In previous section, the electrocatalytic activity of $\text{TiO}_2@\text{TPP-CB}[6]$ was examined without addition of any co-catalyst. In this part, we discuss the effect of insertion of Ni in the form of nickel acetate tetrahydrate easily with grinding $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in powder form with TPP-CB6 and TiO_2 in the system. In most reports on electrocatalysts for HER, platinum is used as the co-catalyst which is a precious metal. Here we have

decided to employ an earth abundant metal, Ni, to study its influence on the catalytic activity of our sample.

The corresponding ink was prepared as Table 3-4. Similar to the preparation method in previous section, the known amount of ink was drop casted on FTO surface and dried at RT. The catalytic activity of samples were studied in KOH electrolyte (0.1 M). The linear sweep voltammetry (LSV) measurements were recorded at scan rate of 10 mV/s.

Table 3-4- Composition of Ni inserted composites

Composite	Nickel acetate tetrahydrate (mg)	TPP-CB[6] (mg)	TiO ₂ (mg)	H ₂ O (μl)	Ethanol (μl)	Nafion (μl)
12%Ni+TiO ₂ @TPP-CB6	2	4	8	250	50	10
12%Ni@TPP-CB6	2	4	-	250	50	10

Another composite was prepared by eliminating TiO₂ from ink as presented in Table 3-4. LSV experiments were performed for the three composites, TiO₂@TPP-CB[6], 12%Ni+TiO₂@TPP-CB[6], and 12%Ni@TPP-CB[6] in 0.1 M KOH electrolyte. According to the polarization curves in Figure 3-18, addition of Ni shifted the onset potential of catalytic reaction to a more positive value of -250 mV vs. RHE and increased the current density, meaning that catalytic activity of electrocatalyst has significantly improved. This can be explained in the way that Ni atoms not only provide active sites for proton reduction, but also may facilitate the electron transfer to the center of porphyrin (Zn²⁺) and consequently increase the hydrogen production rate. Also using an alkaline electrolytes prevent corrosion as well as dissolution of non-precious metals, this can provide an efficient alternative over catalysis in acidic media. Moreover, Ni-based electrocatalysts, owing to their 3d electron configuration which provoke their stability in alkaline electrolytes, are known as the most promising option for being utilized in electrocatalysts for hydrogen evolution reactions[66].

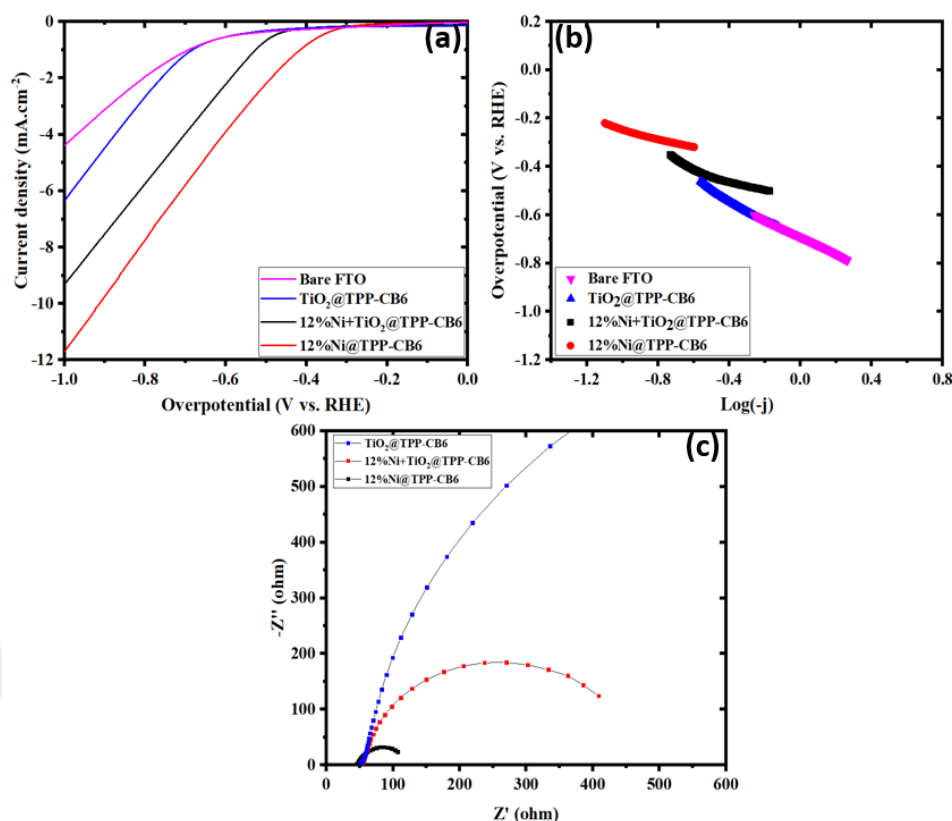


Figure 3-18– Polarization curves, (b) Tafel plots, and (c) Corresponding Nyquist plots (at -0.4 V vs. RHE) for samples containing TPP-CB[6] with/without Ni and/or TiO_2 in 0.1 M KOH electrolyte (pH=13).

Tafel plot is a beneficial method to study the kinetics of an electrochemical system. Therefore, the polarization curves were used to be fitted in equation $\eta = a \times \log(-j) + b$; where a is Tafel slope and b is Tafel constant. As it is shown in Figure 3-18(b), Tafel slopes had declining trend as Ni was added to the composite. Smaller Tafel slope implies that the higher current densities can be achieved at lower overpotentials[88]. Besides Tafel slope, exchange current density is another crucial parameter in evaluating the performance of a catalyst describing the charge transfer rate at equilibrium[89]. As it is presented in Table 3-5, $12\%\text{Ni}@\text{TPP-CB6}$ has the highest exchange current density of $0.363 \text{ mA}\cdot\text{cm}^{-2}$ which can be defined as ease of initiating the reaction.

Table 3-5- Electrochemical parameters for samples containing TPP-CB[6] with/without Ni and/or TiO₂ measured in 0.1 M KOH (pH=13) for HER.

Sample	Onset Potential (mV)	η @ (mV)	Tafel slope (V.dec ⁻¹)	j_0 (mA.cm ⁻²)	R_{ct} (Ω)
TiO₂@TPP-CB6	-550	-683	-0.43	0.193	1727.00
12%Ni+TiO₂@TPP-CB6	-400	-526	-0.27	0.272	375.29
12%Ni @TPP-CB6	-250	-416	-0.19	0.363	68.60

The kinetic studies were further continued using electrochemical impedance spectroscopy (EIS) at -0.4 V vs. RHE in the frequency range of 1 Hz to 10 kHz with 5 mV amplitude in 0.1 M KOH. All three samples exhibited merely one semicircle arc in Nyquist plot (Figure 3-18(c)) which implies the absence of Warburg element. The addition of Ni significantly decreased the semicircle diameter and hence the charge transfer resistance (R_{ct}). The charge transfer impedance of 12%Ni-TPP-CB6 is about seven times smaller than this parameter for 12%Ni+ TiO₂@TPP-CB[6] (the exact R_{ct} values are presented in Table 3-5). Having the lowest R_{ct} suggests fast electrical exchange at electrode-electrolyte interface[90].

For further comparison, series of chronoamperometry experiment were performed to calculated amount of hydrogen produced and corresponding faradaic efficiency. According to the values presented in Table 3-6, amount of H₂ produced and Faraday's efficiency of 12%Ni@TPP-CB[6] overtake the ones for other samples.

Table 3-6- Amount of produced hydrogen and related parameters for samples TPP-CB[6] with/without Ni and/or TiO₂ measured in 0.1 M KOH electrolyte (pH=13).

Sample	Amount of H ₂ produced	Faradaic efficiency	TOF@ η = -0.941 V (s ⁻¹)
TiO₂@TPP-CB6	11.19	81%	-
12%Ni+TiO₂@TPP-CB6	16.27	78%	0.039
12%Ni @TPP-CB6	18.7	85%	0.101

For further examining the influence of this change, double layer capacitance (C_{dl}) measurements were conducted. In this regard, a series of cyclic voltammetry experiments were done in a non-faradaic region at various scan rates in which the emerged current is merely due to the double layer charging. The potential window of 0 – 0.1 V vs. Ag/AgCl and the scan rates of 50 to 100 mV/s were chosen Figure 3-19. Then by plotting $\Delta j (=j_c - j_a)$ versus scan rate and fitting a linear line (Figure 3-19(b,d)), C_{dl} value is given by the slope[83]. Higher slope of 12%Ni@TPP-CB6 demonstrated that this composite could provide more active sites for the catalytic reaction.

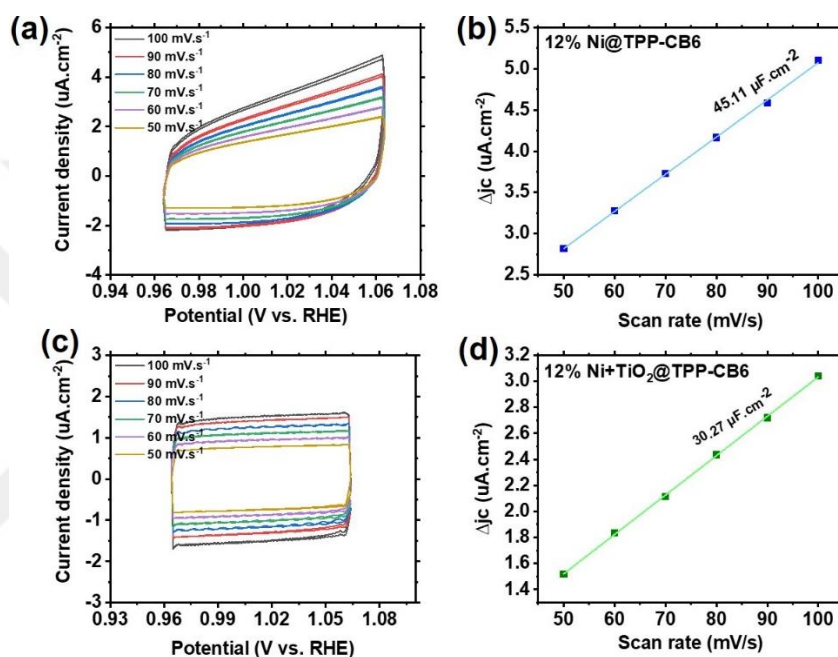


Figure 3-19- (a) CVs of 12%Ni@TPP-CB6 at different scan rates at 0.1 M KOH, (b) Δj at 1.014 V vs. RHE vs. scan rate for 12%Ni@TPP-CB6, (c) CVs of 12%Ni+TiO₂@TPP-CB6 at different scan rates at 0.1 M KOH electrolyte, and (d) Δj at 1.014 V vs. RHE vs. scan rate for 12%Ni+TiO₂@TPP-CB6.

3.3.4 x%Ni@TPP-CB6 composites for HER

In order to find the optimum concentration of Ni, four different concentration of it, 6%, 12%, 23% and 47%, (with respect to TPP-CB6) were studied. Inks were prepared according to Table 3-2 and the surface of FTOs were coated with 20 μl of ink, followed by drying at RT. Electrochemical measurements were again performed in 0.1 M KOH aqueous solution.

Increasing Ni concentration from 6 to 12 resulted in significant rise in current density (Figure 3-20). However, further increase led to reverse response, meaning that electrocatalytic activity started declining. In other words, to reach the current density of 5 mA.cm^{-2} , TPP-CB@12%Ni required -659 V which implies its more active behavior in comparison with TPP-CB@6%Ni (-717 mV), TPP-CB@23%Ni (-749 mV), and TPP-CB@47%Ni (-832 mV). Corresponding Tafel plots (Figure 3-20(b)) are obtained using polarization curves. 12%Ni@TPP-CB6 possessed the lowest Tafel slope with the highest exchange current density. Table 3-7 represents the electrochemical parameters for these composites.

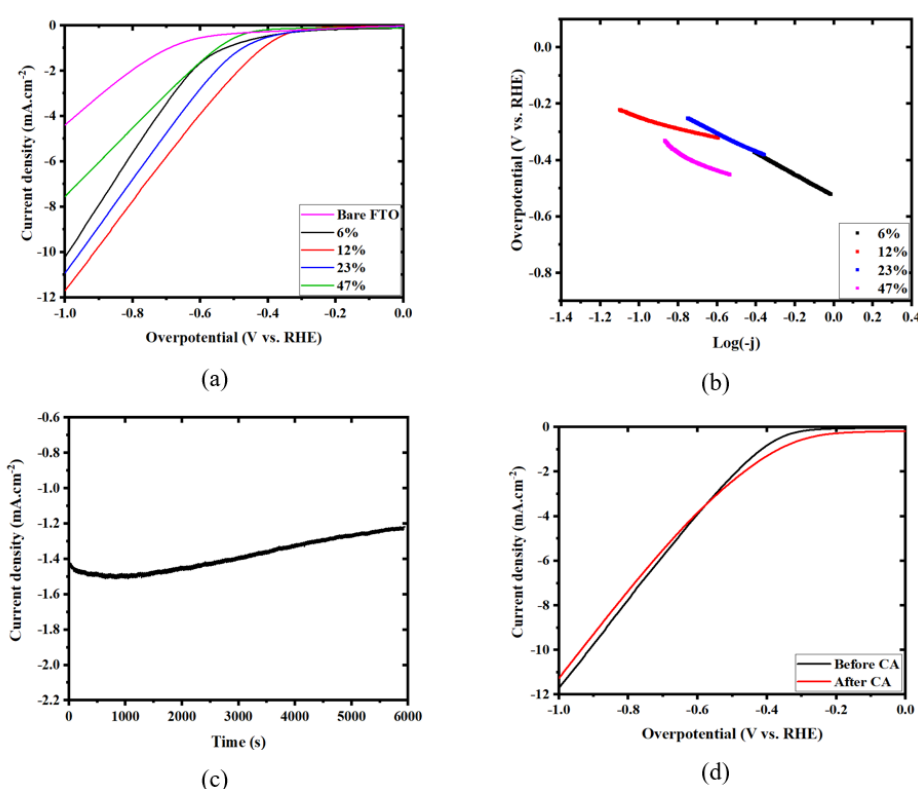


Figure 3-20– (a)Polarization curves and (b) corresponding Tafel plots of samples containing different concentration of Ni toward HER. (Insets: weight percentage of Ni in the composites.), (c) Chronoamperometry experiment performed at -0.4 V vs. RHE in 0.1 M KOH, and (d) Polarization curves before and after CA experiment. All measurements were done in 0.1 M KOH solution with pH 13.

Consistent with exchange current densities, addition of 12% Ni provoked the fastest charge transfer in the system (the smallest R_{ct} value). According to Nyquist plot in Figure 3-21(a), all composites show analogous response, suggesting a similar HER mechanism for them.

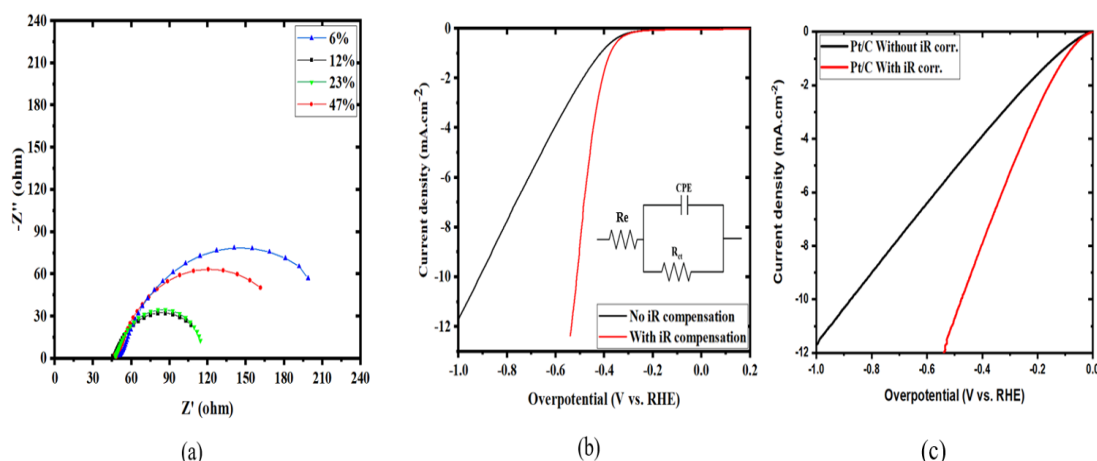


Figure 3-21– (a) Nyquist plots for x%Ni@TPP-CB6 (Inset: weight percentage of Ni in the composites.), and (b) iR-corrected LSV curve 12%Ni@TPP-CB6. EIS results were used to calculate iR compensation. (Inset: the simple Randles equivalent circuit corresponding to 12%Ni@TPP-CB6) (c) LSV curves recorded for PtC (10%) without and with iR correction ($R=40\ \Omega$). All measurements were done in 0.1 M KOH electrolyte (pH=13) solution and EIS were recorded at -0.4 V vs. RHE. (iR correction was applied manually.).

As only one semicircle is observed, the electrochemical system can be modeled using simple Randles equivalent circuit that contains a parallel combination of a capacitance with a resistor in series with another resistor (Figure 3-21(b) inset), where R_e and CPE stand for electrolyte resistance and double layer capacitance, respectively. The absence of Warburg element implies that the electron transfer in the system is fast enough that the reaction is kinetically controlled[91]. Using R_e value from Nyquist plot, polarization curve for the optimum sample was iR corrected. As it is shown in Figure 3-21(b), the potential window shortened significantly and current density of $10\ \text{mA.cm}^{-2}$ can be obtained at a less negative potential of -513 mV compared to -914 mV. For the sake of comparison, the measurements were also performed using commercial 10%PtC. As shown in Figure 3-21(c), the polarization curves are recorded both with and without iR correction. In this measurement, also the correction was applied manually. Overall, based on these results TPP-CB@12%Ni was chosen as the best electrocatalyst for HER in alkaline solution.

Table 3-7- Electrochemical parameters measured toward hydrogen evolution capability of x%Ni@TPP-CB[6] composites in 0.1 M KOH electrolyte.

Sample	Onset Potential (mV)	$\eta@10$ mA.cm ⁻² (mV)	Tafel slope (mV.dec ⁻¹)	j_0 (mA.cm ⁻²)	$j@ \eta = -0.914$ V	TOF@ -0.914 V (s ⁻¹)	R_{ct} (Ω)
6%Ni@TPP-CB[6]	-450	-991	-0.38	0.297	-8.23	0.165	152.3
12%Ni@TPP-CB[6]	-250	-914	-0.19	0.362	-10.0	0.101	68.6
23%Ni@TPP-CB[6]	-380	-955	-0.33	0.311	9.15	0.047	69.4
47%Ni@TPP-CB[6]	-400	---	-0.35	0.222	-6.25	0.016	133.7

As one of the most crucial factors, durability of the electrocatalyst was also examined by chronoamperometry experiment at -0.4 V vs. RHE. TPP-CB@12%Ni composite exhibited perfect stability. Upon applying the Faraday's law, the amount of hydrogen produced was about 18.7 mmol.gr⁻¹.hr⁻¹. Exhibiting similar electrochemical behavior and most importantly, the same onset potential value after CA (Figure 3-20(c)) experiment confirms the stability of our sample.

3.3.5 x%Ni@TPP-CB6 composites for OER

Ni@TPP-CB6 composites were examined for oxygen evolution reaction as well. Measurements were started with linear sweep voltammetry with scan rate of 10 mV/s at RT in 0.1 M KOH (Figure 3-22(a)). All the sample showed OER activity. In addition to a less positive onset potential for 12% Ni@TPP-CB6, this sample could achieve the current density of 1 mA.cm⁻² at only 1.71 V vs. RHE (overpotential of 0.49 V). While other composites required higher overpotentials (0.66, 0.50, and 0.62 mV for 6%, 23% and 47%) and still TPP-CB6 could reach to 1 mA.cm⁻² under the highest potential of 2.1 V vs. RHE. In other words, presence of Ni in the composite could enhance the catalytic activity in alkaline solution where the best performance was observed with addition of 12% (with respect to TPP-CB[6]) of this metal. By comparing the activity of our electrocatalyst with literature, our sample was able to exhibit almost comparable result with previously reported porphyrin electrocatalysts[92][93]. Ni-containing

electrocatalyst can be a catalytic active and cost-effective option for further practical applications.

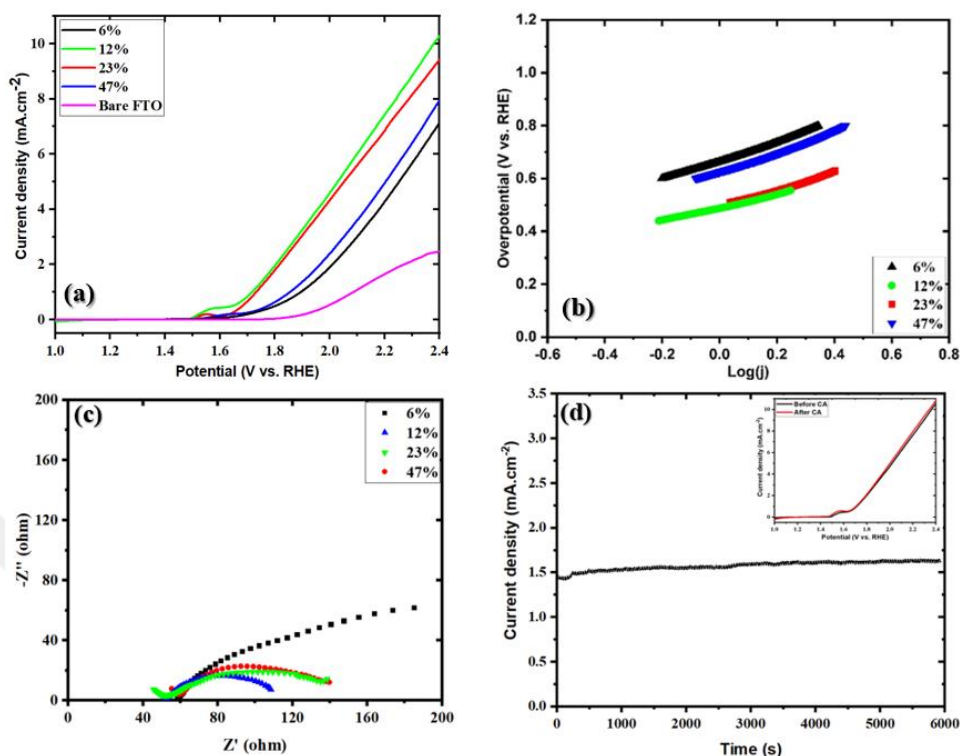


Figure 3-22– (a) Polarization curves for x%Ni@TPP-CB6 (x=6, 12, 23, and 46) at scan rate of 10 mV/s, (b) Corresponding Tafel plots, (c) Nyquist plots of x%Ni@TPP-CB6 performed at overpotential of 0.53 in frequency range of 10 mHz to 10 kHz with amplitude of 5 mV, and (d) Chronoamperometry experiment of 12%Ni@TPP-CB6 at overpotential of 0.53 V for 6000 s in 0.1 M KOH (pH=13) (Inset: Polarization curves before and after CA experiments which show negligible change.). (All measurements were recorded without any iR correction).

The OER kinetics were studied using Tafel plots and electrochemical impedance spectroscopy. First, Tafel parameters were obtained by fitting the linear part of the plot to the equation $\eta = a + b \log(-j)$. According to Figure 3-22(b), high Tafel slopes can be due to presence of $\text{Ni}^{3+}/\text{Ni}^{2+}$ on the surface which are formed during oxidation (oxidation peak at about 1.55 V)[94]. 12% Ni@TPP-CB[6] had the lowest Tafel slope in comparison with other samples. In other words, 12% Ni@TPP-CB[6] exhibited favorable kinetics toward OER and therefore faster O_2 evolution. This confirms the superiority of 12% Ni@TPP-CB6 in water oxidation.

EIS measurements were performed in 0.1 M KOH electrolyte at 1.76 V vs. RHE in frequency range of 0.1 to 100 kHz with amplitude of 5 mV. The Nyquist plots are illustrated in Figure 3-22(c) for all samples. By comparing the diameter of semicircles, it can be understood that 12% Ni@TPP-CB6 owns the fastest kinetics with the smallest charge transfer resistance of about 57 Ω . In conclusion 12% Ni@TPP-CB6 was chosen as an efficient electrocatalyst for oxygen evolution in 0.1 M KOH electrolyte.

Table 3-8- Electrochemical parameters for x%Ni@TPP-CB[6] composites toward OER in 0.1 M KOH (pH=13).

Sample	Onset Potential (V vs. RHE)	η @1 mA.cm ⁻² (V)	Tafel slope (V.dec ⁻¹)	R _{ct} (Ω)
6%Ni @TPP-CB6	1.8	0.67	0.36	127.32
12%Ni @TPP-CB6	1.6	0.48	0.24	57.34
23%Ni @TPP-CB6	1.65	0.50	0.33	92.91
47%Ni @TPP-CB6	1.75	0.62	0.38	86.25

To evaluate the stability of the 12%Ni@TPP-CB[6], chronoamperometry experiment was conducted at 1.72 V vs. RHE for 6000 s which exhibited almost a stable current density response (Figure 3-22(d)). By performing linear sweep voltammetry after this CA experiment, showing the same onset potential was observed which signified the unchanged behavior of our electrocatalyst. The current from CA experiment was applied to faraday's law to obtain amount of produced oxygen. It was calculated that 12%Ni@TPP-CB[6] was able to produce 14.92 mmol.hr⁻¹.gr⁻¹ oxygen with faradaic efficiency of almost 99%. The corresponding electrochemical parameters for these composites are presented in Table 3-8.

3.3.6 Bifunctional electrocatalytic durability of 12%Ni@TPP-CB[6]

The same three electrode cell configuration was used with catalyst coated FTO as the working electrode. The chronopotentiometry experiment (Figure 3-23) was performed in a 0.1 M KOH solution under alternating current densities of -1 and 1 mA.cm⁻² for HER and OER, respectively.

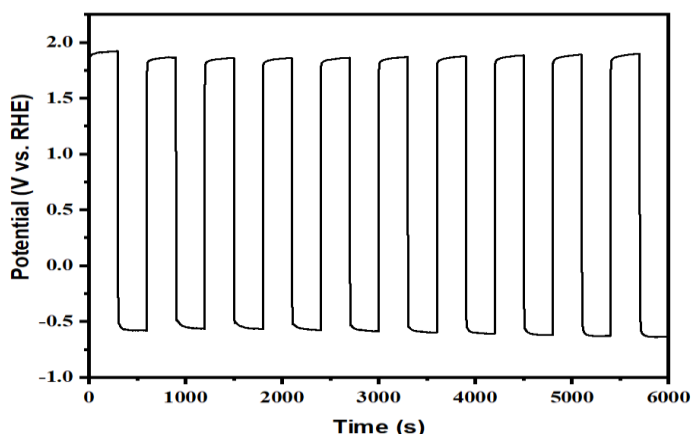


Figure 3-23- Chronopotentiometry for 12%Ni@TPP-CB[6] under alternating current of -1 and 1 mA.cm⁻² measured in 0.1 M KOH electrolyte (pH=13).

The experiment was initiated with anodic polarization and current was switched every 300 seconds. The desired current for water oxidation was achieved at potential of 1.9 V and -0.5 V was required to reach the stable reduction current. These potentials are higher than the previous reported values from LSV curves in previous sections. This can be due to the formed bubbles on the surface of the electrode which were slowly removed during the experiment and resulted in higher required overpotentials. The sample was thoroughly stable during 6000 s experiment with no changes in the potential values which confirmed the durability of 12%Ni@TPP-CB[6] composite as a bifunctional electrocatalyst.

Overall, it was shown that 12%Ni@TPP-CB[6] composite has a bifunctional catalytic activity toward HER and OER in alkaline medium. A high exchange current density of 0.36 mA.cm⁻² as well as charge transfer resistance of 68.60 Ω revealed the fast kinetics of hydrogen evolution reaction. After water electrolysis for 2 hr at -0.4, a faradaic efficiency of 85% for hydrogen production was achieved. After conducting OER experiments, it was observed that 12%Ni@TPP-CB[6] showed perfect oxygen evolution capability. Here also electrochemical impedance spectroscopy showed the fast electron transfer process for this system with small R_{ct} value of 57.34. The faradaic efficiency of 99% was achieved during 2 hours of water oxidation at 1.7 V. observing stable potential values during chronopotentiometry under alternating cathodic and anodic current substantiated the bifunctional electrocatalytic stability of 12%Ni@TPP-CB[6] composite.

Chapter 4

Conclusion

In conclusion, this work studied the potential of conjugated porphyrin supramolecular assembly as a bifunctional electrocatalyst for hydrogen and oxygen evolution. First a composite was prepared using titanium dioxide and the electrochemical experiments were performed in three different acidic, neutral, and basic media to find the proper solution. The composite showed the best catalytic activity and durability in alkaline electrolyte. So the other electrochemical measurements such as linear sweep voltammetry, chronoamperometry, electrochemical impedance spectroscopy and cyclic voltammetry were conducted in this medium.

Next nickel salt was added to the mixture and it was observed that electrocatalytic activity of the new composite has significantly improved. As a result, the onset potential of HER was moved to more positive value of -400 V vs. RHE and the charge transfer resistance subjected to a drastic decrease to 375.29 Ω . By eliminating TiO_2 from the composite, the system demonstrated more favorable kinetics toward HER as R_{ct} value was declined to 68.60 Ω . In this case, the current density of -1 mA.cm^{-2} was achieved at the cost of -0.4 V overpotential while the sample containing TiO_2 required higher overpotential of -0.5 V. As the next step, the effect of various concentration of Ni salt (6%, 12%, 23%, and 47% wrt porphyrin assembly) on the catalytic behavior of the composite was investigated.

After performing linear sweep voltammetries, it was found that 12%Ni@TPP-CB[6] had the most positive onset potential of -250 mV vs. RHE and showed the highest exchange current density of 0.36 mA.cm^{-2} compared with other ratios. These results were consistent with the Nyquist plots where R_{ct} value was the highest for 6%Ni@TPP-CB[6] and the lowest for 12%Ni@TPP-CB[6] composite. Hence 12%Ni was chosen as the optimum concentration leading to the best hydrogen production catalytic activity and fast kinetics.

The oxygen evolution capability of the composites containing Ni (x%@TPP-CB[6]) were also examined in alkaline medium. Again 12%Ni@TPP-CB[6] possessed the best OER catalytic activity. This composite was able to achieve the current density of 1 mA.cm^{-2} at the lowest overpotential of 0.5 V. The impedance spectroscopy experiments and Tafel plots also validated the superiority of this composite with the charge transfer resistance of 57.34Ω . The durability of the sample was demonstrated by performing chronoamperometry experiment in 0.1 M KOH at potential of 1.7 V vs. RHE for 2 hrs and it was calculated that $14.92 \text{ mmol.hr}^{-1}.\text{gr}^{-1}$ O_2 gas was produced during this experiment.

Finally, chronopotentiometry was employed to inquire the bifunctional catalytic stability of the 12%Ni@TPP-CB[6] composite while switching the current between -1 and 1 mA.cm^{-2} . The sample was thoroughly stable after performing this experiment in 0.1 M KOH for 2 hrs.

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