

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**INVESTIGATION OF THE ELECTROCHEMICAL CO₂ REDUCTION
MECHANISM ON TIN ELECTRODES**



M.Sc. THESIS

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Materials Science and Engineering Department

Materials Science and Engineering Programme

JULY 2020

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**KALAY ELEKTROTLAR ÜZERİNDE ELEKTROKİMYASAL CO₂
REDÜKSİYONU MEKANİZMASININ İNCELENMESİ**

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To my family,



FOREWORD

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ABBREVIATIONS

CV	: Cyclic Voltammetry
DFT	: Density Functional Theory
ECR	: Electrochemical CO ₂ Reduction
HER	: Hydrogen Evolution Reaction
OCF	: Open Circuit Potential
PCET	: Proton Coupled Electron Transfer
PEM	: Proton Exchange Membrane
RHE	: Reversible Hydrogen Electrode
SHE	: Standard Hydrogen Electrode



SYMBOLS

$E_{\text{Ag/AgCl}}$	: Potential versus Ag/AgCl reference electrode
$E^0_{\text{Ag/AgCl}}$	: Standard electrode potential with respect to standard hydrogen electrode of saturated Ag/AgCl electrode, 0.1976 V at 25 °C
E_{RHE}	: Potential versus reversible hydrogen electrode
F	: Faraday constant
$FE\%$	: Faradaic Efficiency
$FE_{\text{HCOO}^-}\%$	: Faradaic Efficiency for Formate
n	: The mole number a specific product
Q	: Total charge passed during electrolysis
z	: The required number of electrons for the reduction of CO_2 to a specific product



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INVESTIGATION OF THE ELECTROCHEMICAL CO₂ REDUCTION MECHANISM ON TIN ELECTRODES

SUMMARY

In today's world, one of the biggest concern is climate change. Even though fossil fuels are started to be replaced by renewable energy sources in recent years, this solution turned out to be not sufficient to decrease the accumulated CO₂ in the atmosphere. Increased human population and energy demand escalated the rate of CO₂ emission with a higher rate than environmentally friendly energy sources.

The released CO₂ gas to the atmosphere by human activities is the main factor causing climate change. The increased amount of CO₂ in the atmosphere causes a greenhouse effect that led to an increment in temperature. Thus, the studies concentrate on the CO₂ conversion and storage methods to get rid of the excess CO₂ in the atmosphere.

The conversion of CO₂ is not only useful to eliminate the CO₂ gas in the atmosphere but also the products of this conversion is used as a raw material to produce valuable materials. There are various methods for the conversion of CO₂ such as chemical, thermochemical, electrochemical, biochemical, photochemical, and etc. Among these methods electrochemical CO₂ reduction method has numerous advantages such as no need for heating or pressure, harmless reactants, the possibility to have a carbon-neutral chemical production by supplying energy from renewable energy sources, and convenience to scale-up.

Electrochemical CO₂ reduction is a method in which a CO₂ is reduced on an electrode surface acts as a catalyst. The typical setup for this process involves a cell divided by a proton exchange membrane. The counter electrode and working electrode are located on different sides of the cell. While CO₂ is reduced to various chemicals by taking electrons and H⁺, besides the hydrogen evolution reaction on the working electrode; water-splitting reaction occurs on the counter electrode. There are many products that can be produced by electrochemical CO₂ reduction and their formation potentials are close to each other. In addition, CO₂ is a highly stable molecule due to its linear molecular structures. These two conditions make the use of a catalyst inevitable. The metal catalysts capable of reducing CO₂ are grouped according to their selectivity to specific products. These metals and the products selectively formed on them are Pb, Hg, Tl, In, Sn, Bi, Cd – formate, Au, Ag, Zn, Pd, Ga – CO, Cu – alcohols and hydrocarbons. The optimal binding energy between the catalyst surface and the key intermediate to produce a certain product led to high selectivity.

The aim of this study is to produce selectively formate because of its high energy density and economical value, and its nontoxic nature. Among the metals that are selectively produced formate Sn stands out because of its relatively low price, high availability, innocuousness, and most importantly high selectivity towards formate. Even there are numerous studies published regarding design highly selective Sn-based catalyst to produce formate, a few of them discourse the mechanism providing the high selectivity. However, to design a highly selective and efficient catalyst, one should

understand the factors favoring formate production. Thus, understanding the mechanism will be a breakthrough in electrochemical CO₂ reduction.

In this study, the mechanism of electrochemical CO₂ reduction to formate on the Sn electrode is investigated. At first, the reliable setup was built-up to have replicable and trustworthy results. To achieve the reproducibility, adjustment of the position of the reference electrode and the working electrode with respect to the membrane, stabilization of temperature, the distance between the counter and working electrode, and anode area were done. The working electrode was masked to have an area of 4 cm². However, the results were not reproducible. Following this, the annealing at 150, 180, and 200°C and anode area studies were done. As a result, the annealing has no significant effect on faradaic efficiency in this study. The faradaic efficiencies obtained on 4 cm² were not reproducible, but when the electrode area was decreased to 2 cm² results were reproducible. The increased counter electrode to working electrode area ratio and the more similar sizes of the electrode and membrane, ease the charge transfer and resulted in uniform charge distribution.

Once the reliable setup is achieved, a cyclic voltammetry analysis was done on the pure Sn electrode in CO₂ saturated 0.1 M KHCO₃ electrolyte with pH 6.8. As a result, the reduction peak of tin oxide appeared at 1.0 V vs. Ag/AgCl, and in the literature, the electrochemical CO₂ reduction experiments were done at more cathodic potentials. However, there are many studies indicating that the oxide layer on the tin surface is the key factor governing the high selectivity for formate. To clear up this contradiction, the longtime electrochemical CO₂ reduction experiment was designed to understand the effect of tin oxide on selectivity towards formate. In this experiment, the formate production rates are detected for every ten minutes. The results revealed that in the first ten minutes the produced formate amount was almost 4 times higher than the remaining time intervals. This could be concluded as after the initial reduction of tin oxide the formate production rate decreased dramatically.

Thereafter, 6 different polarization experiments were conducted on pure Sn electrodes to have a better understanding of the relationship between the tin oxide and CO₂ reduction reaction.

In the beginning, the pure Sn electrodes were polarized from open circuit potential to -2 V vs. Ag/AgCl repeatedly until the polarization curves no longer changed. Firstly, this process was done in Ar saturated 0.1 M KHCO₃ electrolyte with pH 8.5. The resulting curve preserved its oxide peak, however, it was slightly reduced. When the experiment was repeated in CO₂ saturated 0.1 M KHCO₃ with pH 6.8, the oxide was greatly reduced. This contrast between two experiments might be originating from the differences in CO₂ presence or pH of the electrolytes. Thus, the final experiment was done in H₂SO₄ added 0.1 M KOH which has a pH of 6.8 but there was no CO₂ or even HCO₃⁻ in the electrolyte. The eventuated curve preserved its oxide peak, and that was more similar to polarization curves obtained in Ar saturated 0.1 M KHCO₃ than the CO₂ saturated 0.1 M KHCO₃. However, it is worth noting that after the first cycle the oxide is reduced even less than the Ar saturated 0.1 M KHCO₃.

The second set of polarization experiments was designed to reduce the tin oxide electrochemically before the polarization. At first, the pure Sn electrodes were reduced at -1.8 V vs. Ag/AgCl for 15 minutes to give enough time to have a full reduction and simulate the real experimental conditions. Then, the polarizations were started at -1 V rather than to open circuit potential to prevent the re-oxidation of the Sn surface, and it continued until the -2 V vs. Ag/AgCl. This process was repeated similar to the

previous set of experiments until the polarization curves did not change anymore. The results were consistent with the experiments that do not involve prior electroreduction. The polarization curves obtained in Ar saturated 0.1 M KHCO_3 with pH 8.5 and H_2SO_4 added 0.1 M KOH with pH 6.8 were similar, but the reduction of the oxide was less in the H_2SO_4 added 0.1 M KOH. In the polarization curve obtained in CO_2 saturated 0.1 M KHCO_3 with 6.8 pH, no oxide peak has appeared. Thus, it can be suggested that the oxide is more prone to be reduced in the presence of CO_2 or HCO_3^- . This experiment proves that the electrochemical CO_2 reduction proceeds with not only CO_2 gas but also HCO_3^- ions in the electrolyte. Additionally, at more cathodic potentials than -1.6 V vs. Ag/AgCl, it was clear that both hydrogen evolution reaction and electrochemical CO_2 reduction reactions become kinetically limited because the slope of the curves become steeper. The steepness of the curves at more negative potentials than -1.6 V vs. Ag/AgCl can be listed as higher to lower, CO_2 saturated 0.1 M KHCO_3 , Ar saturated 0.1 M KHCO_3 , and H_2SO_4 added 0.1 M KOH. Since, as the CO_2 and HCO_3^- amount increases in the electrolyte the reaction becomes more limited, it can be said that the electrochemical CO_2 reduction reaction becomes more limited than the hydrogen evolution reaction.

In conclusion, the two main outcome of this study is that the formate production rate was decreased with the reduction of the tin oxide, and total reduction of tin oxide on the surface is only achieved by the presence of CO_2 in the solution indicating a synergic interaction between tin oxide and CO_2 . Thus, this study reveals the strong relationship between the tin oxide reduction reaction and ECR. In addition, it reveals the missing point in the literature about how tin oxide is affected by the electrochemical CO_2 reduction reaction.



KALAY ELEKTROTTLAR ÜZERİNDE ELEKTROKİMYASAL CO₂ REDÜKSİYONU MEKANİZMASININ İNCELENMESİ

ÖZET

Günümüzde, insanlığı ilgilendiren en büyük sorunlardan birisi iklim değişikliğidir. İklim değişikliğinin en büyük sebeplerinden biriside olarak da insan aktiviteleri sonucu ortaya çıkan yüksek miktarda CO₂ gazı gösterilmektedir. Her ne kadar son yıllarda fosil yakıtlar yerine yenilenebilir enerji kaynakları kullanarak bu gaz salınımı azaltılmaya çalışılsa da atmosferdeki CO₂ gazının yıldan yıla artışı bu girişimin başarısız kaldığını göstermektedir. Üstelik artan insan popülasyonu ve dolayısıyla enerji arzı iklim değişikliği krizini tırmandırmaktadır.

Atmosferde artan CO₂ gazı sera etkisine sebep olmakta ve Dünya sıcaklığında artışa sebep olmaktadır. Bu yüzden bilim dünyası atmosferdeki fazla CO₂ gazından kurtulmak amacıyla CO₂'in dönüştürülmesi ve depolanması çalışmalarına yoğunlaşmıştır.

CO₂'in dönüştürülmesi sadece atmosferdeki fazla CO₂ gazından kurtulunmasını değil, aynı zamanda değerli kimyasalların üretilmesi için CO₂'in hammadde olarak da kullanılmasını sağlar. CO₂'in dönüştürülmesi için kimyasal, termokimyasal, elektrokimyasal, biyokimyasal ve fotokimyasal gibi pek çok yöntem vardır. Ancak bunların içinden elektrokimyasal CO₂ redüksiyonu, uygulama için fazladan sıcaklık ve basınç uygulamasına gerek olmaması, proses girdilerinin zararsız olması, gerekli elektrik enerjisinin yenilenebilir kaynaklardan sağlanması ile karbon-nötr bir proses olma ihtimali ve modüler yapısından dolayı sistemi büyütmenin kolay olması gibi sebeplerle öne çıkmaktadır.

Elektrokimyasal CO₂ redüksiyonu yönteminde CO₂ gazı, katalist olarak görev yapan bir elektrot yüzeyinde indirgenerek farklı kimyasallara dönüştürülür. Bu sistem basitçe bir proton değiştirici membran ile ikiye ayrılmış bir hücreden oluşur. Hücrenin bir tarafında çalışma elektrodu bulunurken diğer tarafta karşıt elektrot bulunur. Katalist olarak görev yapan çalışma elektrodu üzerinde CO₂ elektron ve proton alarak çeşitli kimyasallara dönüşür ve yan reaksiyon olarak da hidrojen oluşum reaksiyonu vardır. Karşıt elektrot üzerinde ise su parçalanarak elektron, proton ve oksijen gazı oluşturur. Elektrokimyasal CO₂ redüksiyonu ile birbirlerine çok yakın oluşum potansiyelleri olan birçok farklı kimyasal üretilir. Bunun yanı sıra, CO₂ lineer bağ yapısından dolayı son derece kararlı bir bileşiktir. Hem bu kararlılığın bozulması için gereken fazladan enerjiyi düşürmek, hem de birbirine çok yakın potansiyellerde oluşan ürünleri seçici olarak üretebilmek için katalist kullanmak zorunludur. Elektrokimyasal CO₂ redüksiyonu için kullanılan metal katalistler seçici olarak ürettikleri ürünlere göre üç grupta incelenebilir. İlk grupta seçici olarak format üreten Pb, Hg, Tl, In, Sn, Bi ve Cd metalleri, ikinci grupta seçici olarak CO gazı üreten Au, Ag, Zn, Pd ve Ga metalleri ve son grupta ise alkol ve hidrokarbonları üretebilme yeteneğine sahip tek metal olan Cu yer alır. Bu metallerin seçici olarak belirli ürünleri üretmesinin altında yatan sebep Sabatier prensibi olarak da bilinen o ürünü üretmek için gerekli olan ara ürünün metal yüzeyine ortalama bir bağlanma enerjisi ile bağlanmasıdır. Bu bağlanma enerjisi çok

olduğunda ara ürün metal yüzeyine adsorplanır ve yüzeyden ayrılmadan önce bir daha reaksiyona girerek farklı ürünlere dönüşür. Öte yandan, bu bağlanma enerjisi az olduğunda ise ara ürün elektron transferi gerçekleşmeden yüzeyden ayrılır ve ürün oluşamaz. Bu sebeple, belirli bir ürünü üretmek için gerekli ara ürün ve metal yüzeyi arasındaki bağlanma enerjisi optimum bir değerde olmalıdır.

Bu çalışmada ise bahsedilen tüm ürünler içinden yüksek enerji yoğunluğu, ekonomik değeri ve zararsız doğasından dolayı üretilmek üzere format seçilmiştir. Formatı seçici olarak üretme yeteneğine sahip metaller arasından ise hem yüksek seçiciliğe sahip olması hem de ucuzluğu, kolay bulunabilirliği ve zararsızlığı sebebi ile araştırma konusu olarak kalay elektrotlar seçilmiştir. Literatürde elektrokimyasal CO₂ redüksiyonu yöntemi ile yüksek seçicilikte format üretmek için kalaya dayanan katalistlerin tasarlanmasına yönelik pek çok çalışma vardır. Bu yöntemler içinde, kalay nanoyapıların farklı tabanlıklar üzerinde oluşturulması, alaşımlama, oksit türevi yüzeylerin oluşturulması gibi birçok yöntem vardır. Literatürde yeni kalay elektrotların tasarlanmasına yönelik fazla sayıda çalışma olsa da bu çalışmaların çoğunda bu tasarımların reaksiyon mekanizmasını nasıl etkileyeceği ve seçiciliği nasıl artıracaklarını öngörmemişler ve deney sonuçlarını yorumlarken artan seçiciliğin sebebini mekanistik olarak açıklamamışlardır. Ancak, yeni bir katalist tasarlanırken kalay üzerinde gerçekleşen elektrokimyasal CO₂ redüksiyon reaksiyonu mekanizması bilinmelidir ki yüksek format seçiciliğine ve verime yol açacak unsurlar tasarıma eklenebilsin. Bu nedenle elektrokimyasal CO₂ redüksiyon reaksiyonunun mekanizmasının tam anlamıyla anlaşılması bu konuda çığır açacak ve sonrasında katalistlerin tasarımında büyük bir yol katedilecektir.

Bu tez çalışmasında Sn elektrot üzerinde elektrokimyasal CO₂ redüksiyon yöntemi ile format oluşum reaksiyonunun mekanizması incelenmiştir. Literatürde, kalay üzerinde yapılan elektrokimyasal CO₂ redüksiyon çalışmaları sonucu faradaik verim %10 ile %90 arasında değişmektedir. Bu durum elde edilen sonuçlarının deney düzeneği ve deney koşullarına önemli derecede bağlı olduğunu göstermektedir. Bu nedenle, deneysel çalışmalara güvenilir bir deney düzeneği kurmakla başlanmıştır. Deney düzeneğinde çalışma elektrodu olarak saf Sn, karşıt elektrot olarak platinize titanyum elektrot ve referans elektrot olarak da Ag/AgCl elektrot kullanılmıştır. Bundan sonra verilecek tüm potansiyeller Ag/AgCl'e göredir. Güvenilir bir deney düzeneği oluşturmak için referans elektrodun çalışma elektroduna göre ve çalışma elektrodunun da ortada yer alan proton değiştirici membranın boyutuna ve yerine göre pozisyonu ayarlanmıştır. Ayrıca sıcaklık, çalışma ve karşıt elektrotların birbirlerine mesafesi ve anot alanı sabitlenmiştir. Çalışma elektrodu da maskelenerek alanı 4 cm² olacak şekilde sabitlenmiştir. Fakat yapılan bir saatlik deneyler sonucunda ortaya çıkan format faradaik verimlerine bakıldığında tekrarlı bir sonuç alınamamıştır. Sonrasında kalay üzerinde kendiliğinden oluşmuş olarak bulunan oksitin özelliklerinin eşitlenmesi için elektrotları 150, 180 ve 200°C sıcaklıklarda 5 saat boyunca tavlایarak ve çalışma elektrodunun alanını 2 cm²'ye düşürerek deneyler yapılmıştır. Bu deneyler sonucunda tavlamanın bu deney düzeneğinde önemli bir etkiye sahip olmadığı görülmüştür, ancak elektrot alanının 4 cm²'den 2 cm²'ye düşürülmesi ile %75 ve %80 arasında değişen tekrarlı faradaik verim sonuçları elde edilebilmiştir. Çalışma elektrodunun alanının düşürülmesi ile artan karşıt elektrot ve çalışma elektrodu alan oranı ve 2 cm² alanın proton değiştirici membranın boyutlarına ve pozisyonuna daha uygun olması, yük transferini kolaylaştırmış ve elektrot yüzeyinde daha homojen yük dağılımı sağlayarak güvenilir ve tekrarlanabilir sonuçlar vermiştir.

Güvenilir bir deney düzeneği kurulduktan sonra, 6.8 pH'a sahip CO₂'e doyurulmuş 0.1 M KHCO₃ elektrolit içinde ve saf Sn elektrot üzerinde dönüşümlü voltametri çalışması yapılmış ve -1.0 V' ta kalay oksitin redüksiyon piki görülmüştür. Litetatürde yapılan neredeyse bütün çalışmalarda elektrokimyasal CO₂ redüksiyon reaksiyonu için elektrotlara bundan daha katodik potansiyeller verilmektedir. Yani reaksiyon öncesinde oksit katmanının redüklenmesi gerekmektedir. Buna rağmen, birçok çalışmada kalay üzerindeki yüksek format seçiciliğinin sebebinin üzerindeki oksit katmanı olduğu savunulmuştur. Bu çelişkiyi açıklamak için 2 saat süren Sn üzerinde elektrokimyasal CO₂ redüksiyon çalışması yapılmış ve bu çalışmada her 10 dakikada bir elektrolitten örnekler alınarak üretilen format miktarı analiz edilmiştir. Sonuçlara bakıldığında ilk 10 dakikada üretilen format miktarının diğer zaman aralıklarında üretilen format miktarından neredeyse 4 kat fazla olduğu görülmüştür. Böylece deney başlangıcında kalay oksitin redüklenmesinden sonra format üretim miktarının önemli ölçüde düştüğü söylenebilir.

Daha sonra kalay oksitin redüksiyon reaksiyonu ve elektrokimyasal CO₂ redüksiyon reaksiyonu arasındaki ilişkinin daha iyi anlaşılması adına 6 farklı koşulda polarizasyon çalışması yapılmıştır.

İlk deneylerde saf kalay elektrot tekrarlı olarak açık devre potansiyelinden -2 V'a kadar ve oluşan polarizasyon eğrileri farklılık göstermeyene kadar polarize edilmiştir. Bu deney öncelikle pH'ı 8.5 olan Ar ile doyurulmuş 0.1 M KHCO₃ elektroliti içinde yapılmıştır. Oluşan polarizasyon eğrilerine bakıldığında ilk çevrimden sonra oksit pikinde bir azalma gözlenmiş fakat pik tamamen yok olmamıştır. Üstelik bu azalma çevrim sayısı arttıkça artmamış sabit kalmıştır. Aynı deney pH'ı 6.8 olan CO₂ ile doyurulmuş 0.1 M KHCO₃ elektroliti içinde yapıldığında ilk çevrimden sonra oksit pikinin büyük oranda azaldığı görülmüştür ancak tamamen yok olmamıştır. Bu iki elektrolitten elde edilen polarizasyon eğrileri arasındaki fark iki nedenden kaynaklanabilirdi. Birincisi CO₂ gazının varlığı ikincisi ise pH farklarıydı. Bu durumu açıklamak için üçüncü bir deney daha tasarlandı. Bu deneyde 0.1 M KOH çözeltisine pH 6.8'e gelinceye kadar H₂SO₄ eklendi. Böylece bu elektrolitte CO₂ redüksiyonuna sebep olabilecek CO₂ gazı ve HCO₃⁻ iyonu bulunmazken elektrolitin pH'ı CO₂'e doyurulmuş 0.1 M KHCO₃ elektroliti ile aynı, yani 6.8'di. Bu elektrolitle yapılan polarizasyon deneyi sonucunda ilk çevrimden sonra oksit pikinde azalma gerçekleşmiş fakat tıpkı Ar'a doyurulmuş 0.1 M KHCO₃ elektrolit içerisinde yapılan deneyden çıkan eğri gibi bu pik yok olmamıştı. pH'ı 8.5 olan Ar'a doyurulmuş 0.1 M KHCO₃ elektrolitinden elde edilen eğri ile pH'ı 6.8 olan H₂SO₄ eklenmiş 0.1 M KOH elektrolitinden elde edilen eğrinin benzer olması ve pH'ı 6.8 olan CO₂'e doyurulmuş 0.1 M KHCO₃ elektrolitinden elde edilen eğrinin bunlardan farklı olması aradaki farkın pH'tan değil CO₂'in varlığından oluştuğunu kanıtlamıştır.

İkinci deney setinde ise polarizasyon öncesinde saf Sn elektrot üzerinde varolan oksit tabakasının indirgenmesi için elektrotlara 15 dakika boyunca -1.8 V uygulanmıştır. Daha sonra polarizasyon açık devre potansiyelinden değil -1 V'tan başlatılarak -2 V'a kadar yapılmış ve polarizasyon eğrileri farklılık göstermeyene kadar bu işlem tekrar edilmiştir. Bu deneylerde açık devre potansiyelinden başlamamanın sebebi Sn üzerinde oksit tabakasının tekrardan oluşmasını önlemektir. Bu deneylerin sonucu da kalaylara polarizasyon öncesinde elektrokimyasal indirgeme yapılmayan deneyler ile tutarlıdır. Ar'a doyurulmuş 0.1 M KHCO₃ elektroliti içerisinde yapılan deney sonucunda oksit piki korunmuş ve yok olmamıştır. Ancak CO₂'e doyurulmuş 0.1 M KHCO₃ elektroliti ile yapılan deney sonucunda oksit piki tamamen kaybolmuştur. Aynı şekilde pH'ı 6.8 olan H₂SO₄ eklenmiş 0.1 M KOH elektroliti ile yapılmış

deneyden elde edilen eğride de oksit piki tıpkı Ar'a doyurulmuş 0.1 M KHCO_3 elektrolitinde olduğu gibi korunmuş ve yok olmamıştır. Ancak bu iki eğri karşılaştırıldığında, oksit pikinin Ar'a doyurulmuş 0.1 M KHCO_3 elektrolitinde daha çok azaldığı görülmüştür. Böylece elektrokimyasal CO_2 redüksiyon reaksiyonunun sadece CO_2 gazı üzerinden değil ayrıca HCO_3^- iyonu üzerinden de yürüyebileceği gösterilmiştir. Tüm bunlara ek olarak, oluşan tüm eğrilerin -1.6 V'tan sonra eğimlerinin arttığı yani kinetik olarak limitlendiği görülmüştür. Bu bölümün eğimi CO_2 'e doyurulmuş 0.1 M KHCO_3 elektrolitinde en fazla, H_2SO_4 eklenmiş 0.1 M KOH elektrolitinde ise en azdır. Elektrolitlerdeki CO_2 ve HCO_3^- oranı arttıkça eğimin de artması reaksiyonun daha çok limitlendiği anlamına gelir. Buradan hareketle de -1.6 V'tan daha katodik potansiyellerde elektrokimyasal CO_2 redüksiyon reaksiyonunun hidrojen oluşum reaksiyonundan daha çok limitlendiği söylenebilir.

Son olarak, bu tez çalışmasının en önemli iki çıktısından birincisi kalay oksitin redüklenmesi ile format üretim miktarının düşmesinin gösterilmesi, ikincisi ise kalay oksitin redüksiyonunun sebebinin elektrokimyasal CO_2 redüksiyon reaksiyonu olduğunun gösterilmesidir. Bir başka deyişle, bu çalışma elektrokimyasal CO_2 redüksiyon reaksiyonu ile kalay oksit redüksiyon reaksiyonu arasında güçlü bir ilişki olduğunu göstermiştir. Buna ek olarak, literatürde kalay oksitin elektrokimyasal CO_2 redüksiyon reaksiyonundan nasıl etkilendiği ile ilgili eksik noktaya parmak basmıştır.

1. INTRODUCTION

The climate change caused by CO₂ emissions from human activities is well-discussed for years by the authorities, scientists, and the general public. Governments, try to find solutions for reducing CO₂ emissions and provide incentives to researchers to decrease the temperature increment in the atmosphere caused by CO₂ emission. These efforts are ensured and supported by international agreements [1].

The research about eliminating the CO₂ from the atmosphere includes basically the capture, conversion, and storage of CO₂ [2].

Electrochemical CO₂ reduction involves the conversion of CO₂ to useful chemicals such as CO, formic acid, hydrocarbons, and alcohols. It has numerous advantages over the other conversion methods. These are: there is no need for increased pressure and temperature, suitability for scale-up by simply increasing the electrode number, low amount of ingredients, and no use of harmful chemicals. In addition, the process can become carbon neutral or negative by using renewable energy sources as an electricity source [3]. The electrodes used for ECR acts as a catalyst by reducing the overpotential and producing selectively certain products. However, the factors determining the product selectivity by explaining the reaction mechanisms on these electrocatalysts are not revealed yet. Thus, in the literature, there are different mechanisms proposed about how CO₂ reduction takes place[4–12].

In this study, the production of formate from CO₂ with ECR is aimed. As it has low toxicity, low price, and high availability, tin electrodes are used for this purpose in many studies [5]. The studies mainly focused on designing new, effective, and selective tin catalysts to produce formate. For this purpose, nanostructures, oxide derived surfaces, alloying and combination with carbon-based nanomaterials methods are widely used [13]. However, we suggest that, prior to design a new catalyst, one should know the mechanism that provides high selectivity and efficiency on specific electrodes, so that the designs can be made to enhance this mechanism. Consequently, the mechanism providing high formate selectivity on tin electrodes was investigated in this study. By building a reliable setup and showing how the result may vary widely

depending on the setup, we were able to point out the importance of the experimental setup to get replicable and trustworthy results, which is not indicated well in the literature. After building a reliable setup, with a long time ECR experiment the importance of the initial tin oxide reduction on the selectivity towards formate is designated. Finally, to investigate the relationship between the tin oxide reduction reaction and ECR reaction, polarization studies were conducted using different solution and reduction potential parameters.

1.1 CO₂ and Climate Change

The amount of carbon on the Earth and its atmosphere does not change because this is a closed system. The changes and movements of the carbon on the Earth are called a carbon cycle given in Figure 1.1. In the Earth, there are carbon sinks that carbon is stored. The main carbon sinks on Earth are rocks and sediments, oceans, atmosphere, and living beings. This stored carbon is released to the atmosphere by the eruption of volcanos, fires, burning fossil fuels, etc. [14].

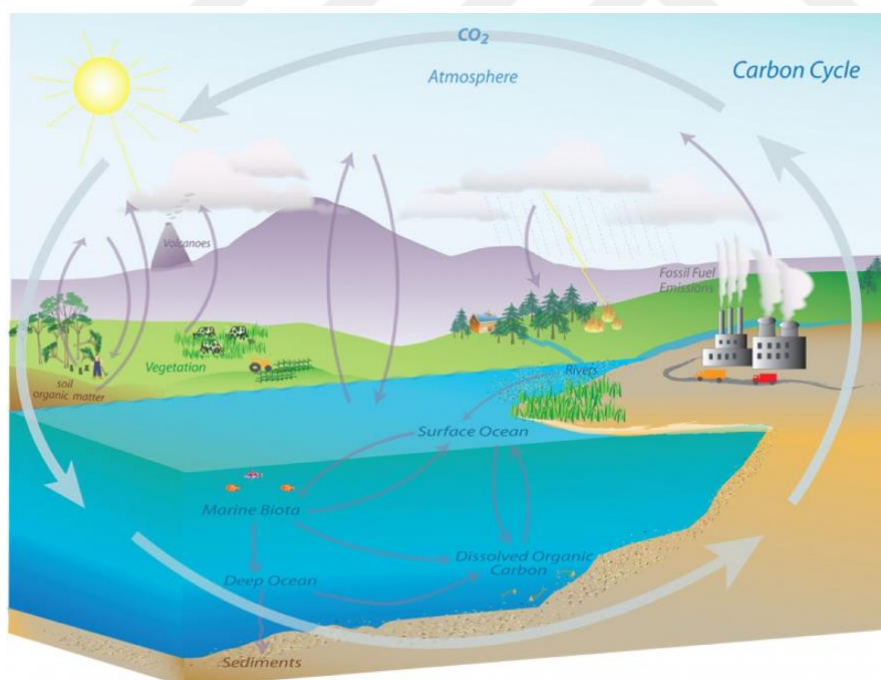


Figure 1.1 : Carbon Cycle Diagram [16].

These natural sources are balanced by nature for many years. However, since the industrial revolution, humans participate in this loop by releasing an excessive amount of CO₂ into the atmosphere. The 87% of emitted CO₂ by human activity is originating

from burning fossil fuels, 9% is from changing land use and destroying forests, and 4% is from industrial activities such as using limestone to make concrete [15].

The temperature of the earth depends on the equilibrium between the absorbed solar energy and infrared radiation turning back to space. The ability of solar energy absorbance of CO₂ gas is very low but it effectively absorbs the infra-red radiation that is supposed to release back to outer space. This incident results in temperature increment on Earth. Also, the increment of the concentration of CO₂ in the atmosphere leads to enhanced absorption of infrared radiation, which is known as the greenhouse effect and it is the reason for climate change [17]. These greenhouse effect of CO₂ in atmosphere is given in Figure 1.2.

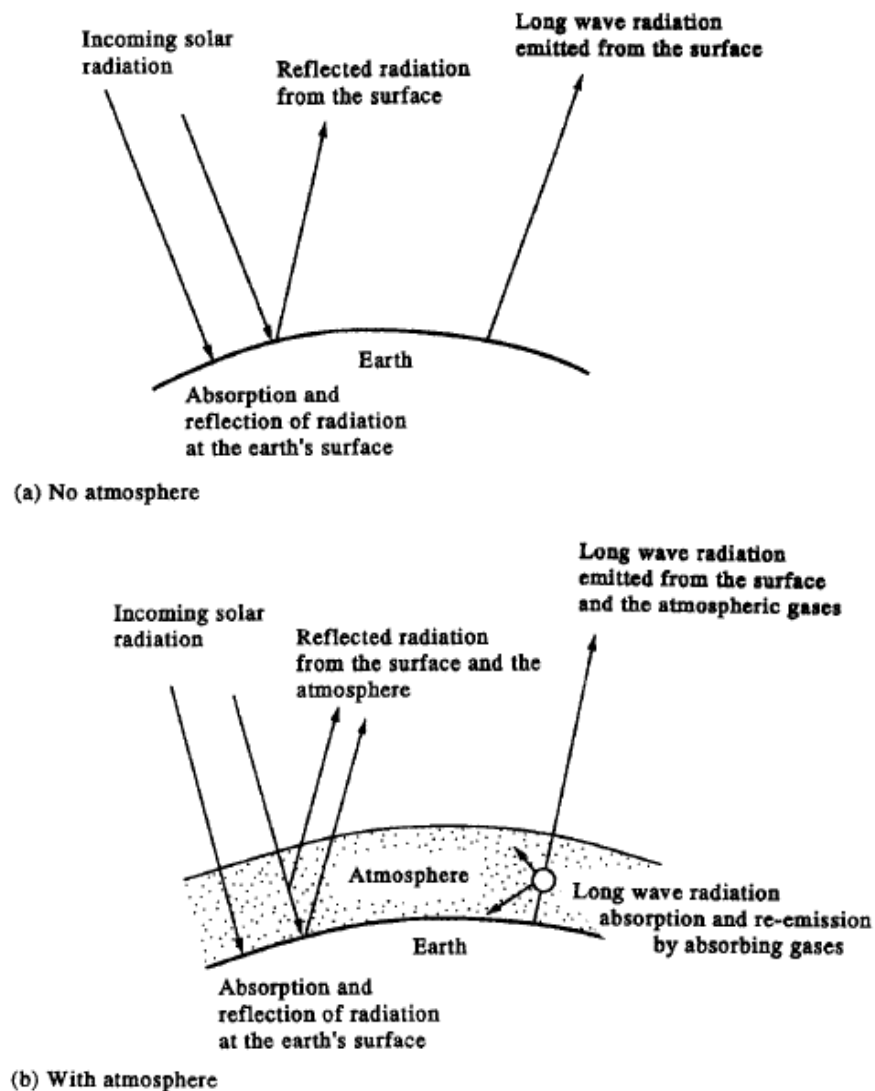


Figure 1.2 : The Greenhouse Effect [17].

Disastrous consequences of climate change will affect human life leading to an increase in sea levels, diseases, and food and water scarcity.

In recent years the CO₂ concentration in the atmosphere reached 415 ppm, which was 280 ppm in the preindustrial era as given in Figure 1.3 [18]. As a result, the studies about CO₂ conversion and utilization is becoming the center of attention.

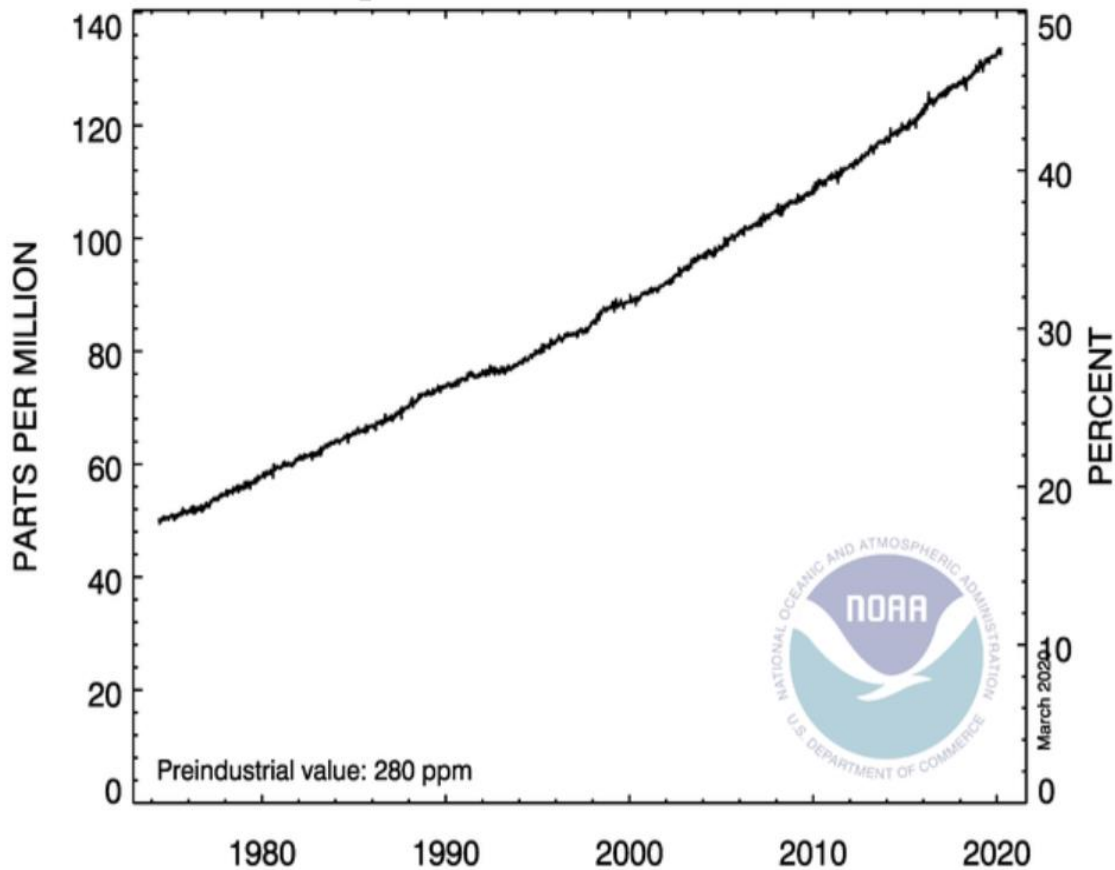


Figure 1.3 : Increase of CO₂ since pre-industrial times (measured at Mauna Loa Observatory) [18].

Four main methods for CO₂ control in Earth are listed below [2] :

- Increasing the energy efficiency to lower the CO₂ emissions
- Using cleaner energy sources instead of fossil fuels
- Capture and storage of the CO₂
- Conversion and utilization of CO₂

1.2 CO₂ Conversion Methods

This thesis is on carbon dioxide conversion, thus other methods of CO₂ control methods are out of the scope of this work and will not be considered in detail.

There are various methods proposed for CO₂ conversion including industrial scale and laboratory scale applications given in Table 1.1. These are radiochemical, thermochemical, photochemical, electrochemical, biochemical, and photoelectrochemical methods. The radiochemical method involves the usage of gamma radiation as an energy source to initiate the reaction between the CO₂ and H₂O. Chemical and thermo-chemical reduction method is used for the production of various products from CO₂. The photochemical reduction of CO₂ uses light energy to produce CO, HCHO, and HCOOH. The electrochemical CO₂ reduction method converts the CO₂ to a vast range of products by applying a potential to the catalyst. Bacteria are also used for biochemical CO₂ reduction method to produce methane [19].

Table 1.1 : CO₂ Conversion Methods [19].

Name of the process	Process
Radiochemical	CO ₂ → HCOOH, HCHO (by gamma radiation)
Chemical Reduction	2Mg + CO ₂ → 2MgO + C
	Sn + 2CO ₂ → SnO ₂ + 2CO
	2Na + 2CO ₂ → Na ₂ C ₂ O ₄
Thermochemical	CO ₂ → CO + ½ O ₂ (in presence of Ce ⁺⁴ and > 900°C)
Photochemical	CO ₂ → CO, HCOOH, HCHO (in presence of hv)
Electrochemical	CO ₂ + xe ⁻ + xH ⁺ → CO, HCOOH, (COOH) ₂ (in presence of eV)
Biochemical	CO ₂ + 4H ₂ → CH ₄ , 2H ₂ O (in presence of bacteria)
Bio-photochemical	CO ₂ + oxoglutaric acid → isocitric acid (in presence of hv)
Photo-electrochemical	CO ₂ + 2e ⁻ + 2H ⁺ → CO + H ₂ O (in presence of hv and eV, Semiconductor)
Bio-electrochemical	CO ₂ + oxoglutaric acid → isocitric acid (in presence of enzyme, eV, and methyl viologen)
Bio-photo-electrochemical	CO ₂ → HCOOH (in presence of hv, enzyme, p-1 nP, eV, and methyl viologen)

Among these methods, the electrochemical CO₂ reduction method stands out due to numerous advantages that will be given in Section 2.



2. ELECTROCHEMICAL CO₂ REDUCTION

Electrochemical CO₂ reduction (ECR) is one of the methods for the conversion of CO₂. The advantages of this method compared to other reduction methods are listed below:

- It can be conducted at room temperature and atmospheric pressure, there is no need for additional heat and pressure sources.
- Consumption of chemicals can be limited to water by recycling of the supporting electrolytes.
- If the energy required for this conversion is supplied from renewable energy sources the carbon footprint of the method is almost zero.
- The modularity of the electrochemical cells allows very easy scale-up [3].

ECR cell mainly consists of two electrodes and an electrolyte. The CO₂ gas is bubbled to the electrolyte and a suitable potential required for CO₂ reduction is supplied through a DC power supply. At the anode, water splits and produces the H⁺ ions and oxygen gas. On the cathode, CO₂ gas is reduced to the other chemicals via electron and proton transfer [20]. Anodic and cathodic compartments of the cell are separated with a PEM membrane for the protection of the reaction products from oxidation.

2.1 Thermodynamics and Kinetics of Electrochemical CO₂ Reduction

Various types of value-added chemicals such as formic acid, carbon monoxide, ethanol, methanol, etc. can be produced by the electrochemical CO₂ reduction process via different reaction pathways including 2⁻, 6⁻, 8⁻, 12⁻ electron transfers [21]. The half-cell reactions and their standard redox potentials ECR products listed in Table 2.1. As can be followed by Table 2.1, the formation potentials of different reduction products are very close to each other. As a result, various products may form under the same applied potential [22]. However, these reactions are kinetically slow and require considerable overpotentials for reaching reasonable reaction rates because CO₂ is a very stable, linear bonded molecule [23]. Thus, cathodic reduction potentials required

to obtain the products are more cathodic than the equilibrium potentials indicated in Table 2.1.

According to the most accepted mechanism for ECR, the rate-determining step is the initial activation of CO₂ by a single-electron transfer that has a standard electrode potential of -1.90 V vs. SHE. Therefore, the hydrogen evolution reaction takes place along with the ECR, because it initiates at potential far below -1.90 V vs. SHE [12]. Thermodynamic calculations show us that it is possible to produce several ECR products and hydrogen during the cathodic reduction of CO₂ on a conductive surface. Thus, if we want to produce specifically an ECR product such as CO, HCOOH, or CH₂, we have to understand the kinetics of this process so that we can selectively produce the required product by decreasing the activation barrier of the related reaction. In the next section, the kinetics of catalytic ECR will be outlined.

Table 2.1 : The half-cell reactions and their standard redox potentials versus standard hydrogen electrode under standard conditions of ECR products at pH = 7 [12].

Reduction Process	E ⁰⁰ (vs SHE, V)
CO _{2(g)} + e ⁻ = [*] COO ⁻	-1.90
CO _{2(g)} + 2H ⁺ + 2e ⁻ = HCOOH _(l)	-0.61
CO _{2(g)} + H ₂ O _(l) + 2e ⁻ = HCOO ⁻ _(aq) + OH ⁻	-0.43
CO _{2(g)} + 2H ⁺ + 2e ⁻ = CO _(g) + H ₂ O _(l)	-0.53
CO _{2(g)} + H ₂ O _(l) + 2e ⁻ = CO _(g) + 2OH ⁻	-0.52
CO _{2(g)} + 4H ⁺ + 4e ⁻ = CH ₂ O _(l) + H ₂ O _(l)	-0.07
CO _{2(g)} + 3H ₂ O _(l) + 4e ⁻ = HCHO _(l) + 4OH ⁻	-0.89
CO _{2(g)} + 6H ⁺ + 6e ⁻ = CH ₃ OH _(l) + H ₂ O _(l)	-0.38
CO _{2(g)} + 5H ₂ O _(l) + 6e ⁻ = CH ₃ OH _(l) + 6OH ⁻	-0.81
CO _{2(g)} + 8H ⁺ + 8e ⁻ = CH _{4(g)} + 2H ₂ O _(l)	-0.24
CO _{2(g)} + 6H ₂ O _(l) + 8e ⁻ = CH _{4(g)} + 8OH ⁻	-0.25
2CO _{2(g)} + 8H ₂ O _(l) + 12e ⁻ = C ₂ H _{4(g)} + 12OH ⁻	-0.34
2CO _{2(g)} + 12H ⁺ + 12e ⁻ = CH ₂ CH _{2(g)} + 4H ₂ O _(l)	+0.06
2CO _{2(g)} + 12H ⁺ + 12e ⁻ = CH ₃ CH ₂ OH _(l) + 3H ₂ O _(l)	+0.08

2.2 The Mechanism for Electrochemical CO₂ Reduction

The most commonly accepted ECR mechanism in an aqueous medium that involves heterogeneous catalysts can be summarized as [24]:

- (1) chemical adsorption of the CO₂ to the active sites of the catalyst surface
- (2) formation of the CO₂⁻ radical anion by one-electron transfer

(3) formation of the product via several electrons and/or proton transfer

(4) desorption of the product from the catalyst surface and diffusion to the electrolyte.

As the ECR is proceeding via multiple electron and proton transfers it is hard to control the product distribution.

The schematic of the commonly accepted complex reaction mechanism is presented in Figure 2.1 [4]. The first and the RDS of the ECR is common for all of the reaction pathways; the activation of CO_2 via one-electron transfer. After that, the binding energy between the $^*\text{CO}_2^-$ intermediate and the surface of the electrocatalyst is the determining factor for the selectivity of the products. If $^*\text{CO}_2^-$ intermediate bonds to the surface via an oxygen atom, the hydrogenation of C atom and one-electron transfer results in HCOO^* formation that is then reduced to HCOO^- , and if it bonds to the surface via the carbon atom, protonation of O atom and one-electron transfer favors the formation of the $^*\text{COOH}$ intermediate which can be reduced to $^*\text{CO}$ and released from the surface by a further reduction to CO . Only on the Cu metal, the $^*\text{CO}$ intermediate can produce CH_4 and other hydrocarbons depending on the applied potential [4].

It should be noted that in Figure 2.1 all ECR reactions begin with the initial electron transfer to CO_2 . This reaction requires -1.9 V vs. SHE in neutral solutions as is stated in Table 2.1. However, in most of the ECR experiments in the literature, and in this study is done at a potential lower than -1.9 V vs. SHE [7,25,26].

In conclusion, since it is not possible to have the initial electron transfer reaction to CO_2 without supplying sufficient thermodynamically energy in other words potential, the mechanism involving the electron transfer reaction to CO_2 is not valid. Thus, in this study proposed mechanisms alternative to this one is compiled.

The pathway that the ECR proceeds show a strong dependence on the metal used as a catalyst. The product distribution resulting from the ECR reaction on the certain catalyst is indicated by the term of selectivity and the selectivity in the ECR shows the ratio of a specific product in all products produced during the reaction according to the given charge.

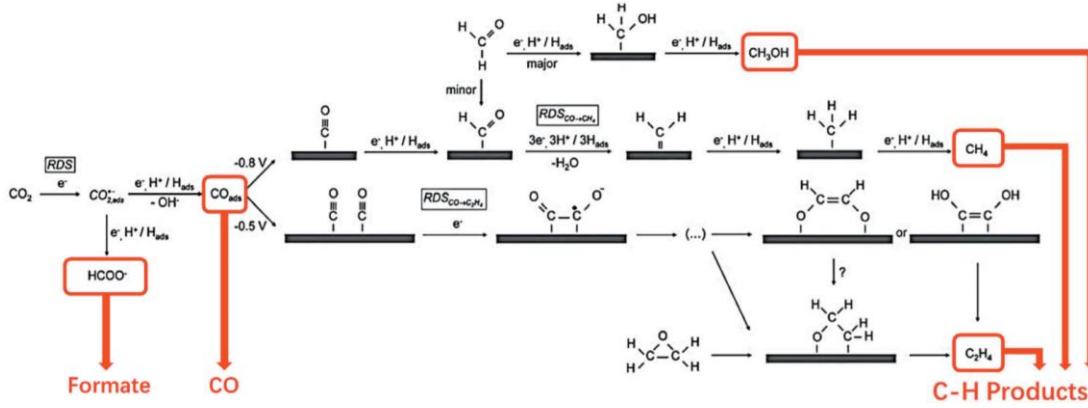


Figure 2.1 : One of the reaction mechanisms for electrochemical CO₂ reduction in aqueous electrolytes based on density functional theory calculations [4].

Faradaic efficiency of a single product is the measure of the selectivity, and it can be calculated as in equation (1.1):

$$FE\% = \frac{z \times n \times F}{Q} \times 100 \quad (2.1)$$

where z is the required number of e^- for reduction to the specific product, n is the number of moles for the product, F is the Faraday constant, Q is the total charge [19].

The differentiation of the product selectivity on the different metals during ECR can be explained by the Sabatier principle. There are several factors that affect the selectivity, however, when the experimental conditions are the same the binding energy of the catalyst to the key intermediates leading to a certain product determines the final product. This relation between the adsorption strength and the catalytic activity is known as the Sabatier principle. It indicates that the intermediate should bond to the catalyst surface with intermediate strength because if it bonds too weak, it cannot bind and react and if it bonds too strong it cannot be desorbed. The binding energy between the catalyst surface and the intermediate is closely related to the structure and defects on the surface. The volcano types of plots are used to indicate optimal catalytic activity [27]. As designated in Figure 2.2 the maximum catalytic activity is at the top of the volcano curve [28].

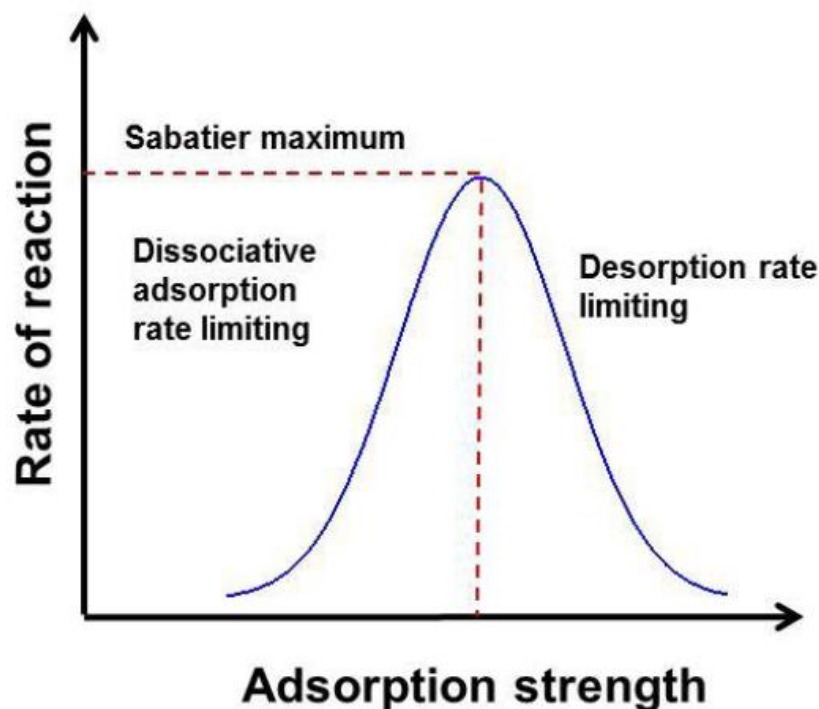


Figure 2.2 : Volcano curve according to Sabatier Principle describes the rate of reaction and adsorption strength relation.

In the theoretical study of Feaster et al., the highest catalytically active metals for formate and CO formation is investigated [8]. Accordingly, the volcano plots are given in Figure 2.3 that designate the optimal binding energy with $^*\text{OCHO}$ intermediate, leading to formate production, is found for Sn, and the optimal binding energy with COOH^* , leading to carbon monoxide formation, is found for Au.

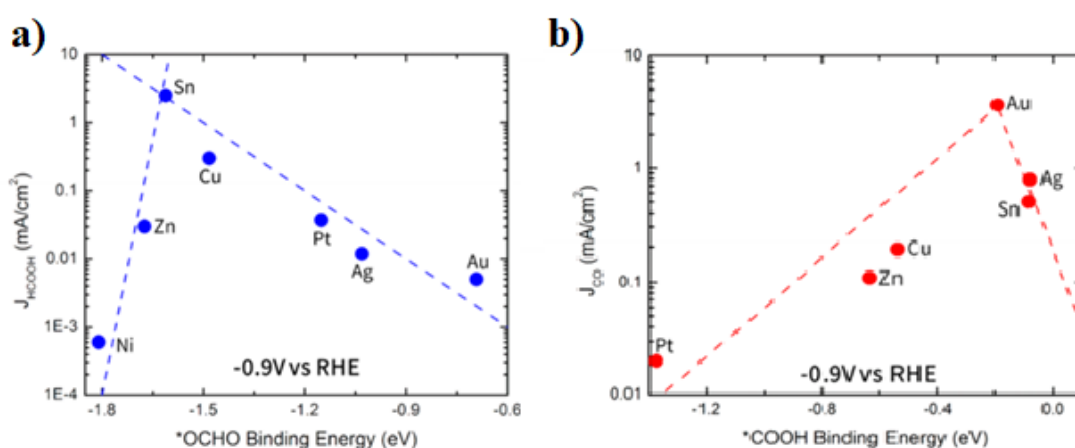


Figure 2.3 : Volcano curves giving the relationship between a) HCOOH partial current density and $^*\text{OCHO}$ binding energy, and b) CO partial current density and $^*\text{COOH}$ binding energy.

Hori et al., classified the metal catalysts in four groups according to their selectivity for various products in Table 2.2. The first group consists of Pb, Hg, Tl, In, Sn, and Bi that selectively produce formate from CO_2 , additional by-products are a small amount of H_2 and CO. Pb, Hg, Tl, and In have the highest, and Sn, Cd, and Bi have relatively lower faradaic efficiency for formate. The second group involves Au, Ag, Zn, Pd, and Ga, and the main product of ECR on them is CO. In addition, HER has a considerable faradaic efficiency on these metals as a side reaction. Especially, Ga has 79% faradaic efficiency for H_2 that makes it an unsuitable catalyst for CO production. In the third group, there is only Cu and that is the only metal catalyst that able to produce C_{2+} products and methane. The metal catalysts of the fourth group are Ni, Fe, Pt, Ti. They are hardly selective to ECR, the highest faradaic efficiency on them is for HER [29].

When the adsorption strengths of the electrodes are identical other parameters may also affect the ECR selectivity. These parameters are the type and pH of the electrolyte, applied potential, temperature, and pressure.

In the literature, aqueous and non-aqueous electrolytes are used for ECR. Since in the scope of this thesis aqueous electrolytes are used, studies conducted in the aqueous electrolytes are mentioned in the literature review.

First of all, the bulk and local pH (on the electrode surface) have a significant influence on selectivity. The pH of the electrolyte may change the equilibrium potentials according to the Nernst equation. In Figure 2.4, the Pourbaix diagram of carbonate- H_2O is given. This diagram designates that in the acidic environment, competing HER occurred at less cathodic potentials. On the other hand, it should be noted that as the pH of the electrolyte increases, CO_2 solubility decreases that results in the decrement of the faradaic efficiency of the total ECR products. Thus, an optimization of the pH of the electrolyte is required to get the highest ECR efficiency [30].

Table 2.2 : Faradaic Efficiencies of the various metal electrodes given in 0.1 M KHCO₃ at 18.5±0.5°C and pH=7 [29].

Electrode	Potential vs. SHE V	Current Density mA cm ⁻²	Faradaic Efficiency, %							
			CH ₄	C ₂ H ₄	C ₂ H ₅ OH	CH ₃ CH ₂ CH ₂ OH	CO	HCOO ⁻	H ₂	Total
Pb	-1.63	5.0	0.0	0.0	0.0	0.0	0.0	97.4	5.0	102.4
Hg	-1.51	0.5	0.0	0.0	0.0	0.0	0.0	99.5	0.0	99.5
Tl	-1.60	5.0	0.0	0.0	0.0	0.0	0.0	95.1	6.2	101.3
In	-1.55	5.0	0.0	0.0	0.0	0.0	2.1	94.9	3.3	100.3
Sn	-1.48	5.0	0.0	0.0	0.0	0.0	7.1	88.4	4.6	100.1
Cd	-1.63	5.0	1.3	0.0	0.0	0.0	13.9	78.4	9.4	103.0
Bi	-1.56	1.2	-	-	-	-	-	77	-	-
Au	-1.14	5.0	0.0	0.0	0.0	0.0	87.1	0.7	10.2	98.0
Ag	-1.37	5.0	0.0	0.0	0.0	0.0	81.5	0.8	12.4	94.6
Zn	-1.54	5.0	0.0	0.0	0.0	0.0	79.4	6.1	9.9	95.4
Pd	-1.20	5.0	2.9	0.0	0.0	0.0	28.3	2.8	26.2	60.2
Ga	-1.24	5.0	0.0	0.0	0.0	0.0	23.2	0.0	79.0	102.0
Cu	-1.44	5.0	33.3	25.5	5.7	3.0	1.3	9.4	20.5	103.5
Ni	-1.48	5.0	1.8	0.1	0.0	0.0	0.0	1.4	88.9	92.4
Fe	-0.91	5.0	0.0	0.0	0.0	0.0	0.0	0.0	94.8	94.8
Pt	-1.07	5.0	0.0	0.0	0.0	0.0	0.0	0.1	95.7	95.8
Ti	-1.60	5.0	0.0	0.0	0.0	0.0	tr.	0.0	99.7	99.7

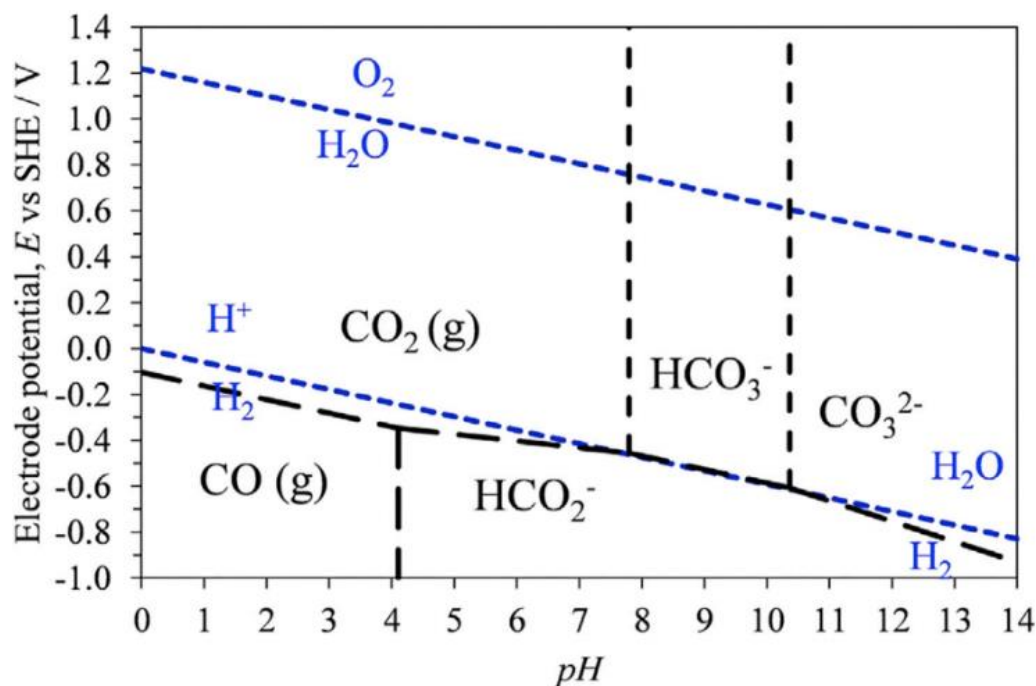


Figure 2.4 : Overlapped pourbaix diagrams of H_2O and Carbonates [30].

Both HER and ECR led to a local increase of pH because of the consumption of H^+ and the production of OH^- ions. Since both of these reactions take place at the catalyst surface, the local pH close to the catalyst surface is higher than the bulk pH of the electrolyte. As the variation of the local pH has an impact on the equilibrium potentials, local pH should also be considered during ECR experiments. Although the buffering effect of the bicarbonate, retards this effect to some extent, even in the case of a flat foil electrode in the 0.1 M $KHCO_3$, a massive difference in the pH of the bulk and near the surface electrolyte is observed. Especially for the copper electrodes, local pH notably influences the selectivity [31]. Koper et al. showed that there are two different pathways on the copper surface to form hydrocarbons. The first one depends on the pH and results in methane and ethylene formation. The second one does not depend on the pH, and it forms ethylene [32,33]. The selectivity of ethylene and ethanol rises with the increasing pH to the expense of efficiency because the concentration of free CO_2 decreases by the transformation to the bicarbonate in the aqueous solution.

The other significant parameter affecting the ECR selectivity is applied potential. There are many studies on the effect of the potential on the ECR selectivity on different catalysts. Qin et al., produced a three-dimensional catalyst by depositing a porous layer of tin on Cu foil by electrodeposition, to investigate the faradaic efficiencies of different products at the -1.0 V, -1.1 V, -1.2 V and -1.3 V vs. RHE. As a result of this

study, they found that -1.2 V vs. RHE gives the highest faradaic efficiency towards formate as 92% [34]. In another study Meyer et al., obtained the maximum faradaic efficiency (82.6%) for formate on nanostructured tin catalysts at -1.8 V vs. SCE [35].

The effects of temperature and pressure on ECR is also investigated in several studies. Hashiba et al., have done a study on Cu catalysts at various temperatures and pressures to investigate their effect on the selectivity of ECR. Firstly, they have done an ECR experiment at 25°C at 1.3, 4, and 9 atm. They have found that the HER is suppressed and CH_4 selectivity increased with the increasing pressure at high current densities. Secondly, they have done an ECR experiment at 1.3 atm at 10°C , 25°C , and 40°C . The maximum faradaic efficiency for CH_4 was 37% at 40°C and 71% at 10°C . Thus, the decrease in the temperature increased the faradaic efficiency towards CH_4 [36].

It should be noted that all variations in the selectivity of ECR depending on these parameters can be different for another catalyst. Thus, in every other research the electrolyte, pH, potential, temperature, and pressure should be optimized by considering the catalyst.



3. ELECTROCHEMICAL CO₂ REDUCTION ON TIN ELECTRODES

It is a fact that there are many products that can be produced by electrochemical CO₂ reduction. Among these, formic acid is one of the most desired ones because of its high economic value and numerous application areas. Formic acid is used as a preservative in agriculture, leather production, rubber production, fuel for fuel cells, and hydrogen storage material [37]. Hg, Pb, Sn, Ir, Bi, are the known electrocatalysts that are selective for formate [29]. Sn stands out among these metals since it is not toxic and low-cost. In addition, it has high selectivity towards formate and high catalytic activity.

Lv et al., used commercial Sn electrode (99% purity) in ECR in CO₂ saturated 0.1 M KHCO₃ at -1.8 V vs. Ag/AgCl, and at the beginning of the experiments measured a FE_{HCOO}-% above 91%. However, the efficiency dropped to 41.7% at the end of the 40 hours. They explained the reason for this decay by the oxidation of the formate at the anode compartment because he did not use a membrane to separate the anode and cathode compartments [38]. Morimoto and co-workers used Sn-coated Cu electrodes with different stoichiometric ratios in ECR experiments. Their results showed that the highest FE_{HCOO}- (89.5%) is obtained for Cu₅₅Sn₄₅ coated Cu electrode and FE decreased with increasing Cu content. However, according to them, FE_{HCOO}-% on bulk Sn electrode was only 63% [39]. Relying on these results they claimed about the synergy of the joint presence of Cu and Sn on ECR. In another similar study, Zhao et. al., investigated the effect of deposition current density of Sn on Cu on FE_{HCOO}-% and the deposition with 5, 10, 15, and 20 mA/cm² current densities resulted in the FE_{HCOO}-% of 64.80, 68.70, 91.70, and 71.1 respectively [40]. Kanan and co-workers have found a FE_{HCOO}- of 19% at -0.7 V vs. RHE in NaHCO₃ electrolyte [7]. Chen et al., have done a study to increase the surface area of the electrode. They have produced Sn nanocones on Cu foil and Cu foam by electrodeposition. As a result of the ECR on these two electrodes at the same potential and electrolyte, the Sn nanocones deposited on Cu foil had 88%, and the Sn nanocones deposited on Cu foam had 90.4% faradaic efficiency towards formate [26].

In conclusion, there are many studies about Sn electrocatalysts, and their faradaic efficiency varies between 10 to 90%, so the faradaic efficiency for formate is extremely dependent on the catalyst structure, and experimental conditions. In the next chapter, the ECR mechanism and effective factors on Sn electrodes will be outlined and discussed [24].

It is obvious that, understanding the reaction mechanism is vital to design a highly efficient catalyst. However, ECR is a very complicated reaction as it involves lots of intermediates, possible active sites, and reaction steps. Prior to the investigation of mechanistic studies, it should be noted that tin has two oxidation states as Sn (II) and Sn (IV), and it forms a native oxide in the air [41]. Since there is no consensus in the literature about the ECR mechanism on Sn electrodes, various reaction mechanisms proposed are summarized in this section. The most accepted mechanism given in Section 2.2 has a serious flaw that will be explained later.

As can be seen in Figure 3.1, tin oxide is reduced to metallic tin below -1.2 V vs. Ag/AgCl. Since ECR requires more cathodic potential than the thermodynamic reduction potential of tin oxide, it is expected that the tin oxide is also reduced to the metallic tin during the ECR [42].

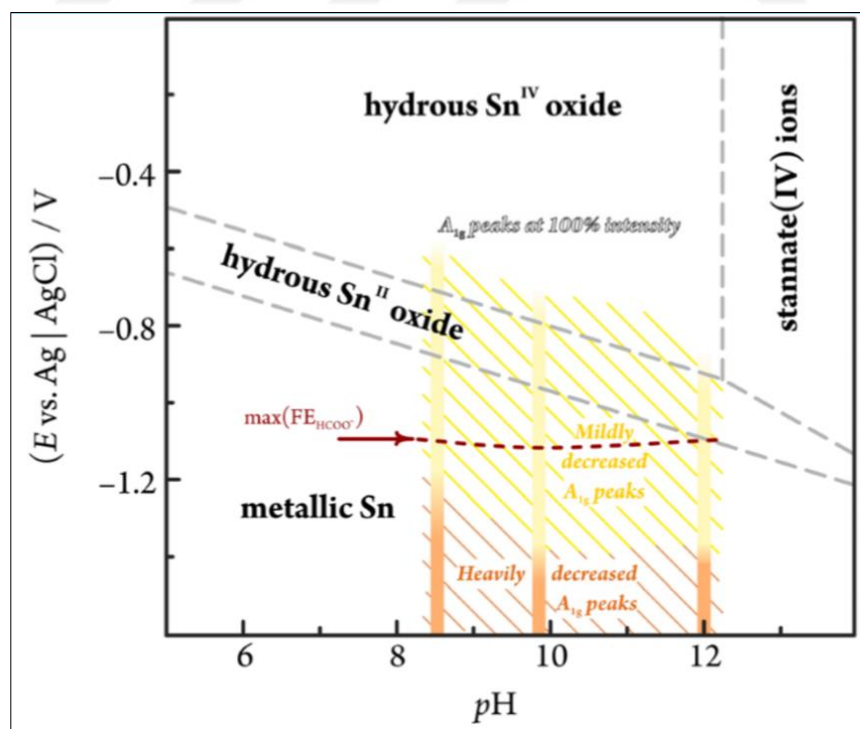


Figure 3.1 : Pourbaix diagram of Sn and its hydrous oxides [42].

Thus, mechanistic studies are focused on whether the oxide layer or the metallic tin is the active site for the ECR. To clarify this point, Kanan et al., investigated the effect of the tin oxide layer on the ECR activity by comparing the FE% towards formate on acid-etched Sn and untreated Sn foils. The results show that acid-etched Sn has only 0.03% faradaic efficiency for formic acid. They noted that, as the Sn surface rapidly grows oxide on it, the small part of the current efficiency towards ECR caused by formed SnO_x prior to the electrolysis. They suggested that the oxide layer on the tin surface stabilize the CO_2^- and favor the CO_2 reduction, however on metallic tin only HER takes place [7].

In addition, Zhang et. al. stated that the oxide layer on the surface of tin is crucial for ECR. They obtain 43% and 84% faradaic efficiency for formate on the etched and untreated Sn surface respectively. Also, they annealed the surface to increase the oxide thickness and it slightly reduces the faradaic efficiency towards formate [25].

Dutta et. al. conducted an operando Raman study to get a better understanding of ECR on the tin surface. They used SnO_2 nanoparticles on a gas diffusion electrode and showed that the oxide is completely removed from the surface after reaching to -1.4 V vs. Ag/AgCl in the 9.7 pH electrolyte, even though the thermodynamic reduction potential is -1.2 V vs. Ag/AgCl. This result indicated that the reduction of tin oxide is kinetically hindered to some extent. Moreover, Dutta and co-workers showed that when the Sn^{II} is present on the surface the highest faradaic efficiency towards formate is obtained, however when the surface is completely reduced to metallic Sn at very cathodic potentials the FE reduces dramatically indicating the FE of ECR is highly dependent of the oxidation state of the tin. Additionally, when they apply a potential more positive than -1.4 V vs Ag/AgCl, the tin oxide is initially reduced but not completely. After that initial reduction a metastable oxide on the surface still exists and does not disappear with the continuing polarization.

For a better understanding of the kinetics of ECR Tafel plots are used in many studies. According to Won's work, the Tafel slopes of Sn foil, Sn dendrite, and heat-treated Sn are 134, 145, and 141 mVdec^{-1} respectively, indicating that the rate-determining step for ECR toward formate formation is initial electron transfer to CO_2 [43]. However, in Kanan's study, the Tafel slopes for HCOOH and CO production on Sn foil with native oxide are 67 and 77 mVdec^{-1} respectively which is close to 59 mVdec^{-1} . The mechanism proposed for this slope is the chemical rate-determining step after a

reversible one-electron transfer to CO_2 to form $\text{CO}_2^{\cdot-}$. The mentioned chemical rate-determining step might be protonation of $\text{CO}_2^{\cdot-}$ or migration to an alternative site on the electrode surface [7]. This result is inconsistent with the initial one-electron transfer to CO_2 as a rate-determining step that is suggested in Won's work. Won et al. claimed a Tafel slope of 137 mVdec^{-1} determined on Sn nanoparticles on the gas diffusion electrode is consistent with the theory of initial one-electron transfer to the CO_2 as the rate-determining step [43].

Other than the claims about initial electron transfer to CO_2 as a rate-determining step and chemical rate-determining step after a reversible one-electron transfer, Feaster et al. proposed a pathway including proton-coupled electron transfer (PCET). They investigated the key intermediates for HCOO^- and CO production on tin electrodes. As a result of the DFT calculations, they suggest that while $^*\text{OCHO}$ is the key intermediate for formate production, $^*\text{COOH}$ is the key intermediate for CO. On contrary to the recent studies that suggest the RDS is the initial one-electron transfer to CO_2 to form $\text{CO}_2^{\cdot-}$, they claimed that the mechanism runs through the first PCET on the oxygen and this leads to the formation of COOH^* or carbon that leads to the formation of $^*\text{OCHO}$ intermediate. Then, the subsequent electrochemical step results in the formation of $^*\text{CO}$ and $^*\text{HCOOH}$ formation, respectively. Finally, these are desorbed from the surface and form CO and HCOO^- [8].

Although the positive role of tin oxide on catalytical activity has been observed in several studies, the number of studies devoted to the explanations for this improvement is limited. In the study of Cui et al., it is noted that the reduction of the SnO layer can result in the formation of oxygen vacancy on the SnO/Sn(112). The computational study they have conducted on the one oxygen vacancy surface indicated that CO_2 can adsorb on the oxygen vacant surface via an O atom. Then, the CO_2 dissociates and forms CO and O. Oxygen fills the oxygen vacancy site and the surface is recovered via the shortening of the O-Sn bond. Simultaneously with this reaction, H_2O in the electrolyte dissociates to two hydroxyl groups by binding of the one O atom to the oxygen vacant site of the Sn surface. The other hydrogen bonds to the next Sn atom. Afterward, it moves to the next O atom on the surface to form a hydroxyl group. CO_2 prefers to react with these hydroxyls and form bicarbonate. Subsequently, bicarbonate is expected to reduce to HCOO^* or COOH^* , but the formation of HCOO^* is thermodynamically more favorable [44]. Likewise, Wang and co-workers suggested

that oxygen vacancies and hydroxyls have a significant effect on catalytic activity towards ECR [6]. As stated earlier, Tafel slopes indicated that the rate-determining step is initial electron transfer to CO_2 to form CO_2^- in the Won's work. They claimed that oxygen abundant surface of tin plays a key role in stabilization of the CO_2^- and other intermediates that also enable formate production [43]. The in-situ ATR-IR study of Bocarsly et al. showed that the ECR runs through the surface bounded tin carbonate species which are present under ECR potentials, and relatively alkaline environments [9]. This intermediate is consistent with the model proposed in Cui's work [44]. Moreover, tin carbonate species disappear when the oxide layer removed from the tin surface which supports the oxide dependence of ECR to formate. The reduction of tin oxide studies showed that the complete reduction to metallic tin occurs at more negative potentials than thermodynamic values. Also, cyclic voltammetry results showed that the reduction of oxide is reversible under ECR conditions. Since the oxide presence is significant for the ECR, they propose an external bias to reoxidize the reduced tin surface. They introduced a mechanism in which the SnO_2 must be reduced to Sn^{II} oxyhydroxides first and then CO_2 reacts with the Sn^{II} oxyhydroxide species and creates tin carbonate species bounded to the surface, and finally, tin-carbonate receives two electrons and proton to form formate which desorbs rapidly from the surface [9]. In Kanan's work [7], the Tafel slope of 74 mVdec^{-1} is ascribed to a reversible one-electron transfer followed by a chemical step, but Bocarsly et al. stated that it can be interpreted as two-electron transfer following the chemical step like in their work [9]. In summary, the proposed mechanism with a chemical step followed by two-electron transfer in Bocarsly's work [9] is inconsistent with the initial electron transfer to the CO_2 and formation of CO_2^- in Won's work [43], but consistent with the Tafel slope stated by Kanan [7]. Recently, Damas et al. conducted computational research that suggests another mechanism. Accordingly, CO_2 is adsorbed to the hydroxyls formed on the tin surface from the O atoms. As a result of the chemical reaction of CO_2 with OH^- , tin carbonate species are formed. Afterward, the tin carbonate species are reduced to formate via PCET. As a result of this process, remaining tin – oxygen on the surface is protonated and healed by the formation of hydroxylated tin [5]. Damas's work agrees with the other studies indicating the chemical reaction takes place between the hydroxylated tin surface and CO_2 followed by electron transfer or PCET [8,9,44].



4. EXPERIMENTAL METHODS

In this work, the investigation of the ECR mechanism and changes in the oxide layer of the tin under various polarization and pH conditions are aimed. At first, a reliable setup was built up to obtain reproducible results. Afterward, in order to understand the relationship between the ECR and the tin oxide layer on the catalyst surface, the cathodic polarization studies have been conducted on tin electrodes in different electrolytes for understanding the kinetics of the competing ECR, HER and tin oxide reduction reactions. To characterize the changes in these reaction rates and the surface of the oxide layer on the tin, the oxide peaks and the slopes of the polarization curves were considered. Additionally, two hours of ECR has done to inspect the changes on the formate production rate depending on time.

4.1 Experimental Setup

The ECR experiments were realized in a custom-made H type cell, which consists of two compartments separated with a membrane (Figure 4.2). Pure tin rods were hot-pressed at 110°C, under a uniaxial pressure of 400 kN, and converted into plates. They were used as a working electrode; platinized titanium mesh electrode was used as counter electrode and Ag/AgCl electrode was used as the reference electrode. Nafion 117 membrane was used as a proton exchange membrane sourced from Sigma-AldrichTM and it was placed between the two parts of the H type cell to prevent the re-oxidation of the products formed in the working electrode compartment. The working electrode compartment had 4 inlets for the working electrode, reference electrode, pH meter, CO₂ gas, and one gas outlet. The working electrodes were mechanically polished with silicon carbide paper down to 2500 grit and cleaned in an ultrasonic bath with acetone for 15 minutes. The masking of the tin plates was done with Tesa[®] 4120 tape. The tin plates with a thickness of 1 mm are masked by covering all of the backside and bottom and upper part of the front side to have 4 cm² and 2 cm² areas. The schematic of the masking is given in Figure 4.1.

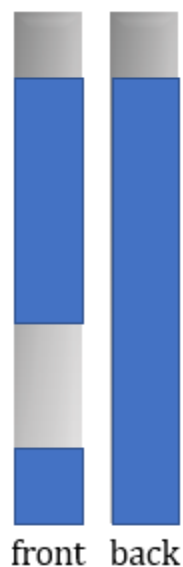


Figure 4.1 : The masking of the pure tin electrodes.

Since we did not see any significant changes due to the annealing with different times and temperatures we did not perform annealing on the tin surfaces to obtain equal conditions before the electrolysis. The H type cell was cleaned ultrasonically for 15 minutes with ultra-pure water before each electrolysis experiment.

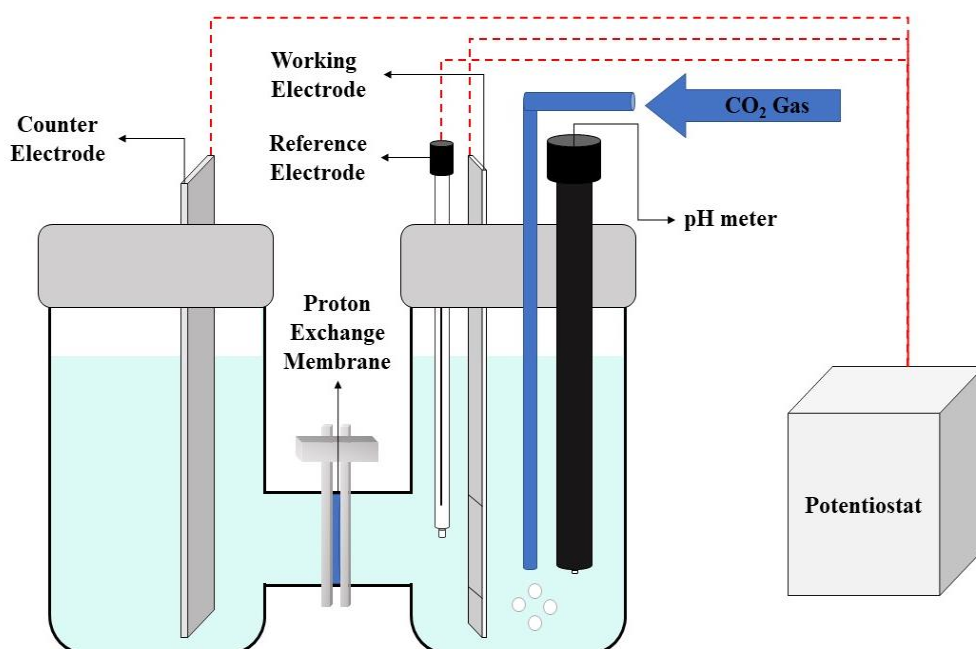


Figure 4.2 : Scheme of the experimental setup for ECR.

4.2 Electrochemical Methods

GAMRY Reference 3000 Potentiostat was used for all electrochemical measurements. The electrochemical measurements were conducted in ambient pressure and temperature. The electrochemical techniques used in this work are cyclic voltammetry, potentiodynamic cathodic polarization, and potentiostatic electrolysis. All potentials in this study are given with respect to Ag/AgCl electrode.

4.2.1 Cyclic voltammetry

Cyclic voltammetry (CV) is an electrochemical technique in which the potential is scanned between two potentials forward and backward completing a cycle, and cathodic and anodic peaks give the redox reactions [45]. In this study, CV measurement was done to determine the oxidation and reduction potentials of the tin electrode and to distinguish the CO₂ reduction and HER potentials. CV measurements were done in H type cell at 200 mV/s and 400 mV/s scan rates, both in Ar saturated (pH=8.5) and CO₂ saturated 0.1 M KHCO₃ (pH=6.8) and electrolyte. 4 cm² tin was used as a working electrode and platinized titanium electrode as the counter electrode. The potentials window was selected between 0.2 V vs. Ag/AgCl and -1.8 V vs. Ag/AgCl.

4.2.2 Potentiostatic electrolysis

In this study, the constant potential of -1.8 V was applied to the working electrode in CO₂ saturated 0.1 M KHCO₃ with pH 6.8. Time-dependent ECR experiments were done for 2 hours, and a 1 ml sample was taken from catholyte for every ten minutes and analyzed with Ion Chromatography. After the experiments, the charge was calculated from the area under the current – time curve for the faradaic efficiency calculations.

4.2.3 Cathodic polarization

The tin electrodes were cathodically polarized in different electrolytes for understanding the contribution of the tin oxides on cathodic polarization behavior. The electrolytes used in the polarization study are Ar saturated 0.1 M KHCO₃ with pH 8.5, CO₂ saturated 0.1 M KHCO₃ with pH 6.8, and H₂SO₄ added 0.1 M KOH with pH 6.8.

Two sets of experiments were designed for each electrolyte, in the first one, the electrodes were polarized from open circuit potential to -2 V vs Ag/AgCl then the polarization is turned off and the potential of the electrode switched back to open circuit. After waiting at open circuit potential for 10 sec. cathodic polarization is initiated again. This cycle was continued until the stabilization of the cathodic polarization behavior. The scan rate used in these experiments was 5 mV/sec.

In the second set of experiments, the pure tin electrodes were reduced electrochemically prior to the polarizations to have a better understanding about the real experimental conditions that cannot be obtained when polarizing the electrodes with the scan rate of 5 mV/sec, since there might be not enough time to have a complete reduction of tin oxide that occurs during the long-time electrolysis experiments. Thus, firstly -1.8 V vs. Ag/AgCl was applied to the working electrode for 15 minutes aiming to reduce the pre-existing tin oxide layer, and then the electrode is polarized from -1 V vs. Ag/AgCl to -2 V vs. Ag/AgCl. Using a scan rate of 5mv/sec. After reaching 2 V, the potential of the electrode is switched to -1 V (without scanning) and then polarized to 2 V by scanning. This procedure is continued until obtaining a stable cathodic polarization curve.

4.3 Product Analysis

Ion Chromatography is a technique that separates the ionic species consists of different columns. At first, the ions are separated by passing through the ion exchange resin-containing column, then identified by their retention time according to their conductivity. [46] In this work, only the liquid products formed because of ECR is analyzed with Ion chromatography. The model of IC used in this study was 930 Compact IC Flex by Metrohm AG equipped with Metrosep A supp 17 – 250/4.0 column. IC was calibrated to detect formate, acetate, and citrate. The samples taken from the catholyte were diluted with ultrapure water with a ratio of 1:100.

5. RESULTS AND DISCUSSION

5.1 Reliable Setup

The literature review in Section 3 showed the strong dependency of the faradaic efficiency on the experimental setup. Thus, for this study, the first step was the preparation of the reliable setup that gives consistent and reproducible results. At the beginning of the study, the experimental conditions are equalized for each experiment. These conditions were the position of the reference electrode, temperature stabilization, stabilization of the distance between the counter and working electrode, anode area, and adjustment of the position of the working electrode with respect to the membrane.

First, the Ag/AgCl reference electrode is positioned to right in front of the working electrode at a very close distance to minimize the IR drop caused by the solution resistance. Then, the temperature of the solution is kept in the range of 18-20°C. The distance of the counter and working electrode was 30 mm for each experiment. Finally, the working electrode is positioned right across the proton-exchange membrane for an even distribution of current on the cathode. The anode size was kept constant as 15 cm² in all experiments.

At first, the working electrode area was 4 cm². As can be seen in Table 5.1, the faradaic efficiencies towards formate varied from 10 to 65% under these experimental conditions. Equalizing of the conditions as stated earlier was not enough to obtain reproducible results.

Table 5.1 : FE_{HCOO}-% results of the ECR experiments conducted with 4cm² electrode area.

Replication Experiment No	Treatment	Working Electrode Area (cm ²)	Faradaic Efficiency for Formate (%)
1	Mechanical Polishing	4	41
2	Mechanical Polishing	4	16
3	Mechanical Polishing	4	11
4	Mechanical Polishing	4	34
5	Mechanical Polishing	4	65

The aforementioned studies indicate that the properties of the oxide layer on the tin surface are the key parameter that affects the faradaic efficiency towards formate[5,7,9,25,35]. Hence, the reason for unreproducible results of the experiments might have been caused by the differences in the oxide layers of tin electrodes. These differences could originate from the thickness or oxidation state of the oxide. Thus, to equalize these properties pure tin electrodes were annealed prior to the ECR experiment. To investigate the effect of annealing 4 sets of experiments are designed and given in Table 5.2.

Table 5.2 : Faradaic efficiencies for formate of the ECR experiments with different pretreated and surface area electrodes.

Experiment No	Treatment	Working Electrode Area (cm ²)	Faradaic Efficiency for Formate (%)
1	150°C 5h Annealing	4	46
2	150°C 5h Annealing	4	65
3	150°C 5h Annealing	4	65
4	180°C 5h Annealing	2	74
5	180°C 5h Annealing	2	79
6	180°C 5h Annealing	2	78
7	200°C 5h Annealing	2	76
8	200°C 5h Annealing	2	80
9	200°C 5h Annealing	2	76
10	Mechanical Polishing	2	75
12	Mechanical Polishing	2	82
13	Mechanical Polishing	4	64

As given in Table 5.2, pure tin samples were annealed at 150, 180, and 200°C for 5 hours.

The first set of the experiment was conducted with the annealed tin foils at 150°C for 5 hours and the working electrode area is determined as 4 cm². However, ECR experiments for these electrodes although gave higher faradaic efficiency for the formate, have not resulted in consistent and reproducible faradaic efficiencies. Thus, the reproducibility of ECR has not been achieved.

Then, the pure tin samples were annealed at 180°C for 5 hours, and the electrode area was reduced to 2cm² to obtain a similar active area with the proton-exchange membrane. In addition, the counter electrode to the working electrode ratio is increased by reducing the working electrode area from 4 cm² to 2 cm². In the literature, it is suggested to have a counter electrode area at least 10 times higher than the working

electrode area to have uniform current distribution and reduce the uncompensated resistance [47,48]. In this case, faradaic efficiency towards formate was varied in a small range of 74-79%, so the results were reproducible. For the third set of experiments, pure tin electrodes were annealed at 200°C for 5 hours, and the electrode area was determined as 2 cm². This set of experiments was distinctive for understanding the effect of annealing temperature because the electrode area was the same as the previously mentioned 180°C annealed samples. As a result of these experiments, the faradaic efficiency for formate was varied between 76-80% which had no significant difference from the 180°C annealed samples with 2cm² area.

Finally, to deeply understand whether the annealing or the electrode was providing the reproducibility, 2 cm², and 4 cm² electrodes without a heat-treatment were used for ECR. The 2 cm² tin electrode without a heat-treatment has resulted with 75% faradaic efficiency towards formate that was consistent with the other 2cm² electrodes with the heat-treatment. On the other hand, 4cm² electrodes without a heat-treatment have the faradaic efficiencies varied in a wide range from 10 to 70%. In conclusion, these experiments showed that the working electrode area is the key parameter governing the reproducibility of the experiments. On the contrary, annealing temperature has no significant effect on the faradaic efficiency towards formate in ECR experiments for the duration of experiments used in this study.

In conclusion, an optimized setup with replicable faradaic efficiency results was obtained with a 2 cm² working electrode area. Further experiments were done in this optimized setup.

5.2 Cyclic Voltammetry

Cyclic voltammetry is applied to the pure tin electrodes to understand the electrochemical behavior of the electrode in the CO₂ saturated 0.1 M KHCO₃ electrolyte with pH 6.8 and given in Figure 5.1. During the anodic polarization, there are two peaks belonging to the +2 and +4 oxidation state of tin at -0.657 V and -0.437 V vs. Ag/AgCl respectively. The peak observed at -1.0 V vs Ag/AgCl is indicating the reduction of the tin oxide to the metallic tin. The reduction peak of the tin electrode appears as a single peak however is supposed to be two separate peaks belonging to the reduction of the two oxidation states of pure tin. Delgado et al. explained this as that the second reduction peak appears when the scan rate is high enough [49].

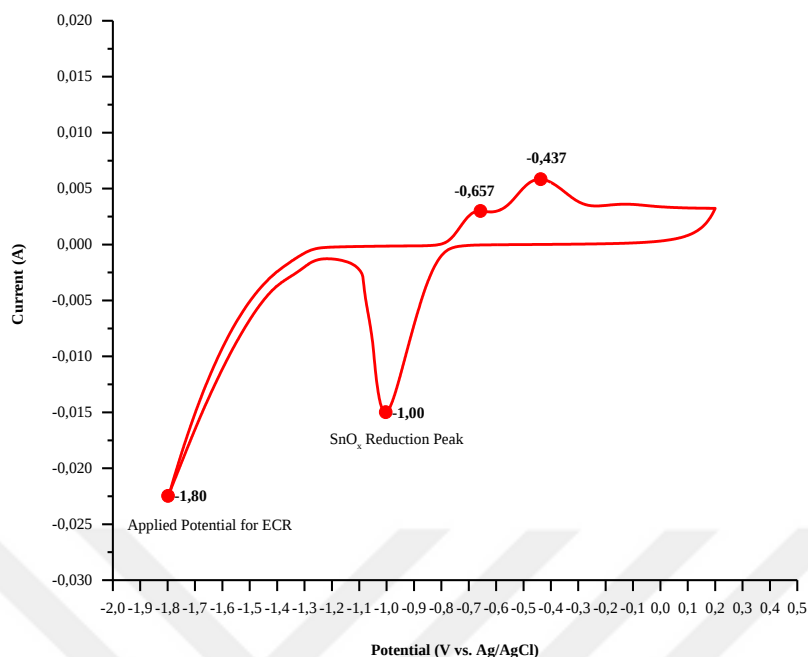


Figure 5.1 : Cyclic Voltammetry of the pure tin electrode in CO₂ saturated 0.1 M KHCO₃ with pH 6.8.

During cathodic polarization after the reduction peak of tin oxide, the downward curve is formed between the -1.26 V and -1.8V vs. Ag/AgCl. In this region, there is a contribution of both HER and ECR reaction according to Damas et al. [5].

As a result, the tin oxide's reduction is a reversible reaction. The cyclic voltammetry curve of tin electrode in CO₂ saturated 0.1 M KHCO₃ electrolyte shows that the oxide layer of the pure tin electrode is started to be reduced at less negative potentials than the ECR potentials. Thus, during the ECR process, the tin oxide is also reduced along with CO₂ and H⁺.

5.3 Time-dependent Formate Production

In the literature, there are numerous studies indicating the importance of the oxide layer on the tin is essential for obtaining high faradaic efficiencies towards formate [7,25,50]. However, our findings from the cyclic voltammetry in Figure 5.1 showed that the tin oxide should start to be reduced prior to the ECR reaction, because the reduction of tin oxide occurs in -1.0 V vs. Ag/AgCl and the ECR experiments mostly were done in -1.8 V vs. Ag/AgCl. Thus, based on these, the question raised was how tin oxide can be the reason for high faradaic efficiencies towards formate while it

supposed to be reduced before ECR reaction. To answer this question, an experiment was designed in which the products were analyzed in every ten minutes during 2 hours ECR in CO₂ saturated 0.1 M KHCO₃ with pH 6.8. In this way, the faradaic efficiency variation during these time intervals and overall time were investigated. There is no other study in the literature that investigates the variation of faradaic efficiency by taking multiple samples during a long-time ECR experiments and relates that to the oxide dependence of faradaic efficiency for formate.

The time-current density graph of the 2 hours long electrolysis experiment is given in Figure 5.2. The current density during the ECR experiment remained stable.

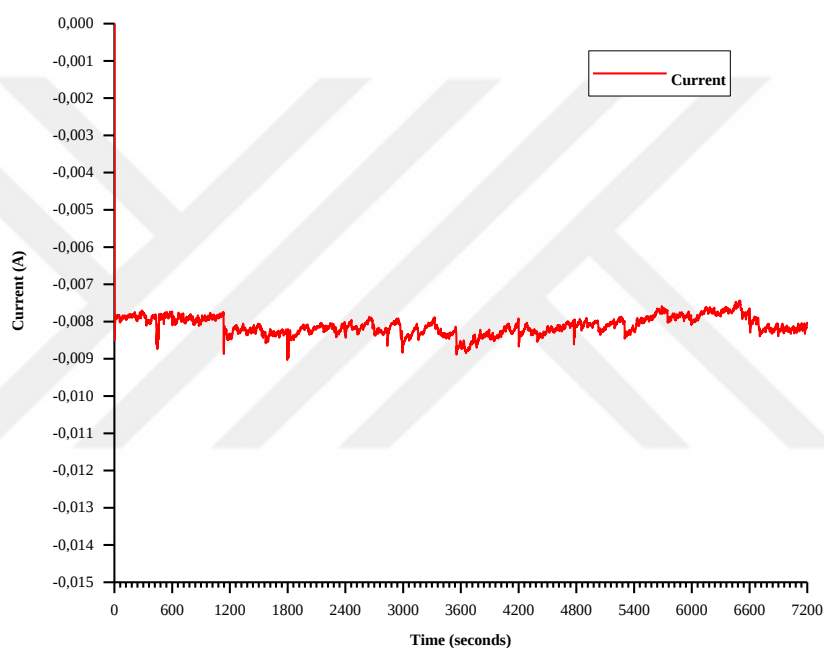


Figure 5.2 : The time – current density graph of 2 hours long ECR experiment at -1.8 V vs. Ag/AgCl in CO₂ saturated 0.1 M KHCO₃ with pH 6.8.

The produced formate amount during the ECR electrolysis is given in Table 5.3. As can be seen in Table 5.3, the produced formate amount was 2.1965 mg in the first 10 minutes that is considerably high comparing the remaining time intervals. After the first 10 minutes, the formate production rate decreased and remained stable. This can be attributed to the effect of tin oxide reduction that decreases the formate production rate. Since tin oxide is thermodynamically not stable at -1.8 V vs. Ag/AgCl, it is expected to reduce in this ECR experiment. It can be said that the presence of tin oxide or the reduction reaction of tin oxide may favor formate production as a result of ECR.

Table 5.3 : Produced formate amount and passed charge in ten minutes time intervals during 2 hours long ECR on the pure Sn electrode in CO₂ saturated 0.1 M KHCO₃ (pH=6.8).

Time Interval (minutes)	Charge (C)	Formate amount (g)
0-10	-4.30	0.0021965
10-20	-4.45	0.0005523
20-30	-4.79	0.0006300
30-40	-4.71	0.0006705
40-50	-4.76	0.0006820
50-60	-4.69	0.0006884
60-70	-4.63	0.0007386
70-80	-4.67	0.0007289
80-90	-4.66	0.0007183
90-100	-4.69	0.0007698
100-110	-4.69	0.0007990
110-120	-4.71	0.0007707

5.4 Cathodic Polarization Studies

The polarization study was done in three different electrolytes to understand the function of CO₂ and its reduction reaction on the oxide layer on pure tin catalysts. To differ the reaction potentials on the metallic tin surface and tin surface with native oxide layer two curves are overlaid in Figure 5.3. The first curve belongs to a pure tin with a native oxide layer in CO₂ saturated 0.1 M KHCO₃ electrolyte with pH 6.8. The second curve belongs to a metallic tin electrode that is obtained by polarization at -1.8 V vs. Ag/AgCl for 15 minutes in CO₂ saturated 0.1 M KHCO₃ electrolyte with pH 6.8 before polarization.

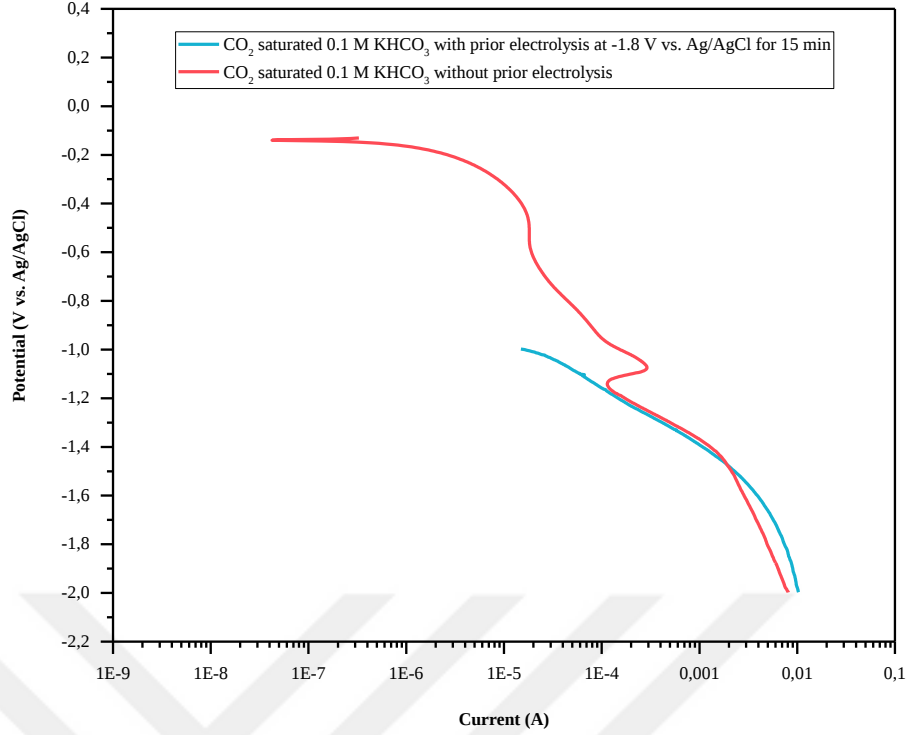


Figure 5.3 : The overlaid polarization curves of metallic Sn and Sn with a native oxide layer in CO₂ saturated 0.1 M KHCO₃ electrolyte with pH 6.8.

There are three reduction reactions involved in these electrochemical experiments and these are, (i) reduction of tin oxide, (ii) ECR, and (iii) HER. Thus, the potentials of all these reactions were subject of several studies. Cho and co-workers made an oxidation study of pure tin via electrochemical reduction analysis in borate buffer electrolyte with pH 8.4 [41]. The reduction potentials of SnO, SnO₂ and Sn(OH)₂ in borate buffer with pH 8.4 are given in Table 5.4.

Since in this study used electrolytes have pH of 6.8, the equilibrium and measured potentials mentioned in Cho's work converted for pH 6.8 to ease the comparison, these are given in Table 5.4. The conversion was done according to RHE because the measured potential with RHE is independent from the pH. Conversion equation between the RHE and Ag/AgCl electrode is given in equation (5.1) [51]:

$$E_{RHE} = E_{\frac{Ag}{AgCl}} + 0.059 pH + \frac{E_{Ag}^0}{\frac{Ag}{AgCl}} \quad (5.1)$$

Additionally, the HER potential on the pure Sn is measured as -1.22 V vs. Ag/AgCl, and the converted potential for pH 6.8 is -1.13 V vs. Ag/AgCl [41].

Table 5.4 : Equilibrium and measured reduction potentials of tin oxides with different oxidation states according to Ag/AgCl reference electrode in pH of 8.4, 6.8, and 8.5 [41].

Potential (V vs. Ag/AgCl)	SnO	SnO ₂	Sn(OH) ₂
Equilibrium Potential in pH 8.4 Borate Buffer	-0.7955	-0.8266	-0.8090
Measured Potential in 8.4 pH Borate Buffer	-0.972	-1.10	-
Equilibrium Potential in pH 6.8	-0.70	-0.73	-0.7146
Measured Potential in pH 6.8	-0.877	-1.01	-

The equilibrium potentials of the possible ECR reactions are given in Table 5.5 [12]. These potentials are designated on the overlaid polarization curve of metallic Sn and Sn with native oxide layer curves obtained in CO₂ saturated 0.1 M KHCO₃ electrolyte in Figure 5.4. To identify the reactions on the polarization curves taken in this study, to have an idea of the experimental potentials of the reactions described above.

Table 5.5 : The equilibrium potentials vs. Ag/AgCl of possible ECR reactions in electrolytes having a pH of 6.8 and 8.5 [12].

Reduction Reaction	Equilibrium Potential in pH=6.8	Equilibrium Potential in pH=8.5
$\text{CO}_{2(\text{g})} + 2\text{H}^+ + 2\text{e}^- = \text{HCOOH}_{(\text{l})}$	-0.80	-0.90
$\text{CO}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{l})} + 2\text{e}^- = \text{HCOO}^-_{(\text{aq})} + \text{OH}^-$	-0.62	-0.72
$\text{CO}_{2(\text{g})} + 2\text{H}^+ + 2\text{e}^- = \text{CO}_{(\text{g})} + \text{H}_2\text{O}_{(\text{l})}$	-0.72	-0.82
$\text{CO}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{l})} + 2\text{e}^- = \text{CO}_{(\text{g})} + 2\text{OH}^-$	-0.71	-0.81

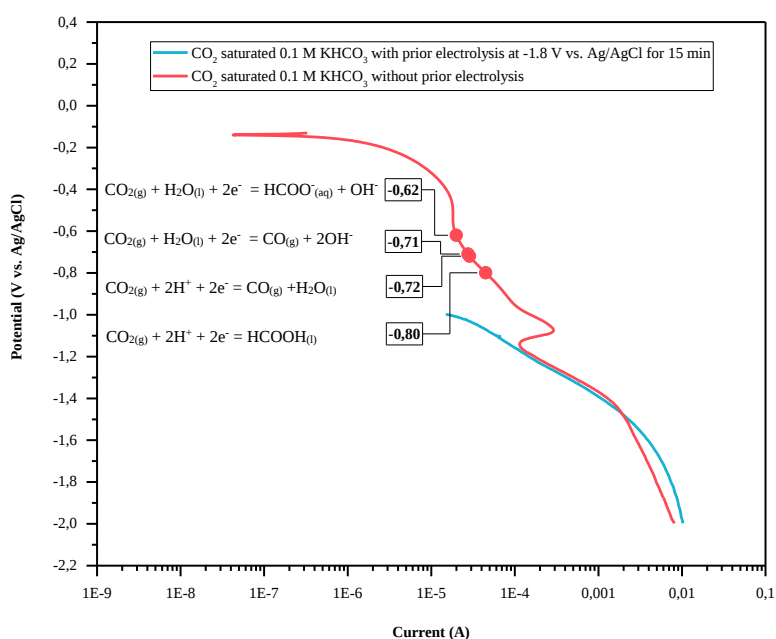


Figure 5.4 : Equilibrium potentials of related ECR reactions [12].

Feaster et al. [8], in their detailed study determined the potentials and potential ranges of the possible reactions that may occur during ECR on tin. These are given in Table 5.6 According to their study at the potentials more anodic than -1.04 V vs. Ag/AgCl the only reaction occurring on the pure tin surface is the reduction of the tin oxide. Between the -1.04 and -1.19 V vs. Ag/AgCl, in addition to the reduction of tin oxide, HER and ECR to formate started. In this potential interval, HER is the dominant reaction. The exact starting potentials of HER and ECR is not stated in the study. CO is first detected at -1.19 V vs. Ag/AgCl. The reactions between the -1.19 and -1.40 V vs. Ag/AgCl are SnO_x reduction, HER, and ECR to formate and CO. Faradaic efficiency for CO is maximum at -1.36 V vs. Ag/AgCl as 17%. ECR to formate becomes the dominant reaction at -1.40 V vs. Ag/AgCl. The maximum faradaic efficiency towards formate is 70% at -1.60 V vs. Ag/AgCl. At the potentials that are more cathodic than -1.6 V vs. Ag/AgCl, ECR becomes mass transport limited, and HER turn into be a dominant reaction again [8]. These potentials are designated on the overlaid polarization curves obtained in CO_2 saturated 0.1 M KHCO_3 electrolyte of metallic Sn and Sn with native oxide in Figure 5.5.

Table 5.6 : Detected reactions occurred on the pure tin electrode in 0.1 M KHCO_3 electrolyte at varying potentials according to Feaster's study [8].

Potential Interval (V vs. Ag/AgCl)	Reaction
Above -1.04	Only SnO_x reduction
-1.04 – -1.19	SnO_x reduction HER (dominant) ECR to HCOO^-
-1.19 – -1.40	SnO_x reduction HER (dominant) ECR to HCOO^- ECR to CO (max FE of 17% at -1.36V)
-1.40 – -1.60	SnO_x reduction HER ECR to HCOO^- (dominant, max FE of 70% at -1.60V) ECR to CO
Below -1.60	ECR becomes mass transport limiting

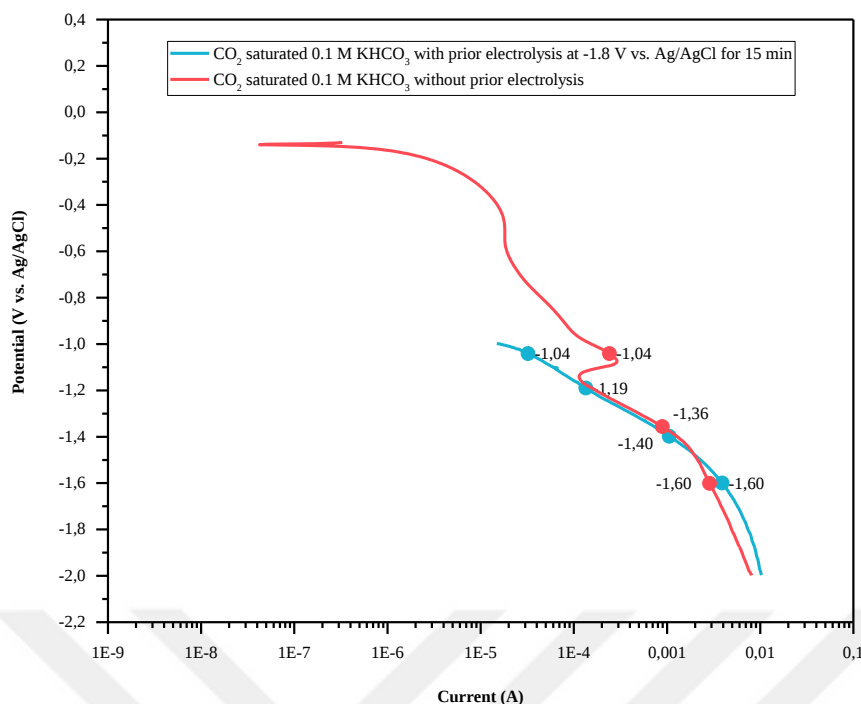


Figure 5.5 : Experimental potentials of related reactions on overlaid curves of metallic tin and tin with native oxide layer according to Feaster's study [8].

Combination of potentials of the Feaster's study and our experimental result of the electrodes with and without oxide layer verified the findings of Feaster. It is clear from the figure that the only reaction occurring on the tin electrode with the native oxide layer until the -1.0 V vs. Ag/AgCl is the reduction of the tin oxide layer. This potential is identified as the reduction of tin oxide in the cyclic voltammetry curve that is given in Figure 5.1. The current increment at this potential is attributed to the reduction of tin oxide. After this potential, two polarization curves become very similar because both surfaces are in reduced form at more cathodic potentials than -1.0 V vs. Ag/AgCl. After the -1.5 V vs. Ag/AgCl, the slope of both curves increases. This could be an indication of the suppressed ECR or HER. Feaster et al., designated that at the potentials more cathodic than the -1.6 V vs. Ag/AgCl ECR reaction becomes mass transport limited [8]. Hence, the suppressed reaction should be ECR due to the mass transport limitation.

5.4.1 Polarization curves without prior constant potential electrolysis

At first, the polarization of pure tin electrodes was conducted without prior constant potential electrolysis. Thus, all of the electrodes used in Section 5.4.1 has a native oxide layer on them at the beginning of the polarization. The polarizations started with OCP to -2 V vs. Ag/AgCl with the scan rate of 5 mV/sec. Thus, in the range of these

potentials, the electrochemical behavior of pure tin electrodes with the native oxide layer was investigated.

First of all, the polarization of the pure tin electrode was obtained in Ar-saturated 0.1 M KHCO_3 electrolyte. This polarization curve is given in Figure 5.6. This experiment was done to understand the behavior of pure tin electrode in 0.1 M KHCO_3 in the absence of CO_2 gas.

As can be seen in the first cycle the tin oxide reduction peak is at -0.89 V vs. Ag/AgCl and the peak current passing in that potential is 573 μA . In the first cycle, after the oxide reduction peak, there is a region between the -0.97 V and -1.29 V vs Ag/AgCl that there is no current increment even the potential is increased.

After the first cycle, the potential of oxide reduction is reduced to -1.167 V vs. Ag/AgCl, and the current passing in that potential is reduced to 305.7 μA . This result indicates that the oxide is began to get reduced after the first cycle but it is not reduced completely because a plateau of current still existed in the potential range of SnO_x reduction. The shape of the CV remained constant after 6th cycle. The remaining cycles were not given in for the sake of better understandibility of the Figure 5.6.

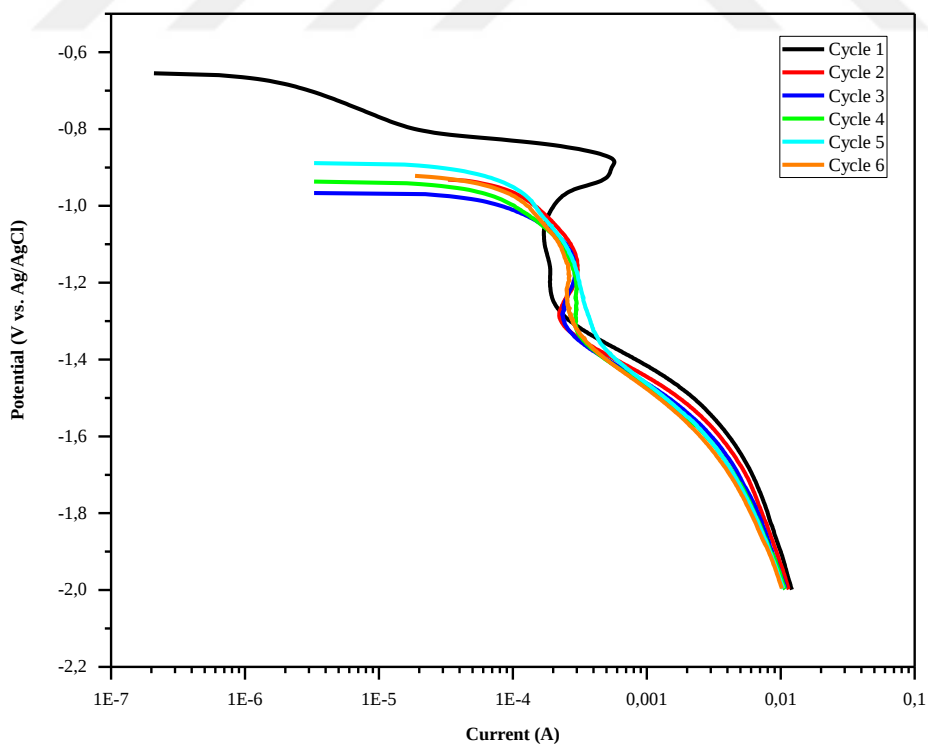


Figure 5.6 : Polarization curves of the pure tin catalyst in Ar saturated 0.1 M KHCO_3 electrolyte with pH 8.5 taken from OCP to -2 V vs. Ag/AgCl.

As it can be seen from Figure 5.7, the first cycle differs from the first cycle obtained in the Ar-saturated 0.1 M KHCO_3 . It is because that the first cycle obtained in CO_2 saturated 0.1 M KHCO_3 electrolyte does not have the region appeared in the first cycle of Ar-saturated 0.1 M KHCO_3 between -0.97 and -1.29 V vs. Ag/AgCl that the current stops increasing while the potential increases. In the first cycle, the oxide reduction peak is at -1.074 V vs. Ag/AgCl and the peak current is 290.9 μA . Unlike Ar-saturated 0.1M KHCO_3 electrolyte with pH 8.5, in CO_2 saturated 0.1M KHCO_3 , after the first cycle, the tin oxide peak is significantly decreased and looks like a bump. The oxide peak has remained stable after the 6th cycle and it was present until the 50th cycle.

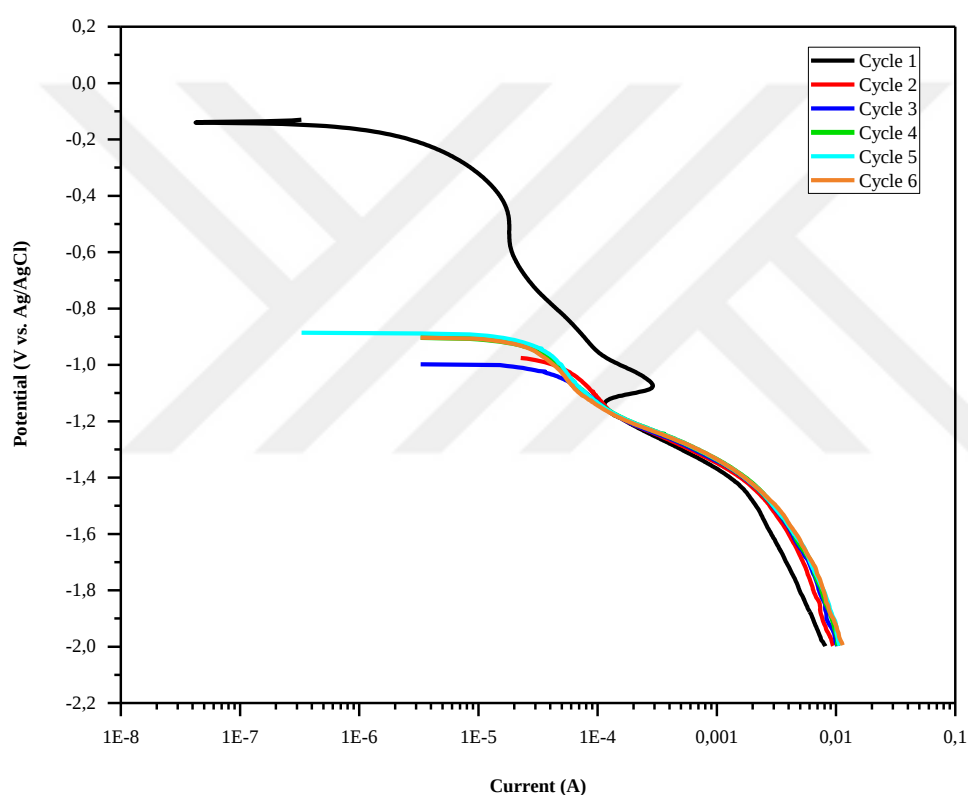


Figure 5.7 : Polarization curves of the pure tin catalyst in CO_2 saturated 0.1 M KHCO_3 electrolyte with pH 6.8 taken from OCP to -2 V vs. Ag/AgCl.

As mentioned before, Ar saturated 0.1 M KHCO_3 has 8.5 pH, on the other hand, CO_2 saturated 0.1M KHCO_3 has 6.8 pH. Thus, this difference between the polarization curves in Ar saturated and CO_2 saturated 0.1 M KHCO_3 electrolyte might be due to the two reasons. These reasons were: (i) pH difference between them or (ii) bubbling CO_2 gas to the 0.1 M KHCO_3 may support the tin oxide reduction. To understand why the oxide is reduced more in CO_2 saturated 0.1 M KHCO_3 electrolyte another experiment is designed.

In the third experiment, H_2SO_4 added to 0.1 M KOH electrolyte to set its pH to 6.8. Thereby, the pH of the electrolyte is equalized with the CO_2 saturated 0.1 M KHCO_3 . If the reason for the higher rate of reduction of tin oxide is that the pH then CO_2 saturated 0.1 M KHCO_3 and the H_2SO_4 added 0.1 M KOH electrolyte with pH 6.8 would have given the same result.

In Figure 5.8, the first six cycles of polarization curves of the pure tin electrode are given. In the first cycle, the oxide reduction peak is at -0.990 V vs. Ag/AgCl, and the maximum current is 435.6 μA . The first polarization cycle obtained in H_2SO_4 added 0.1 M KOH with a pH of 6.8 is similar to the first polarization cycle obtained in Ar-saturated 0.1M KHCO_3 electrolyte. The region that the current does not increase with the increasing potential in Ar-saturated 0.1M KHCO_3 electrolyte is between -0.97 V and -1.29 V vs. Ag/AgCl was also present in the first cycle of H_2SO_4 added 0.1 M KOH electrolyte with pH 6.8 between the potentials of -1.0 V and -1.3 V vs. Ag/AgCl. After the first cycle, the oxide is reduced but a plateau is still preserved in this region. The oxide reduction peak was stable after the 6th cycle.

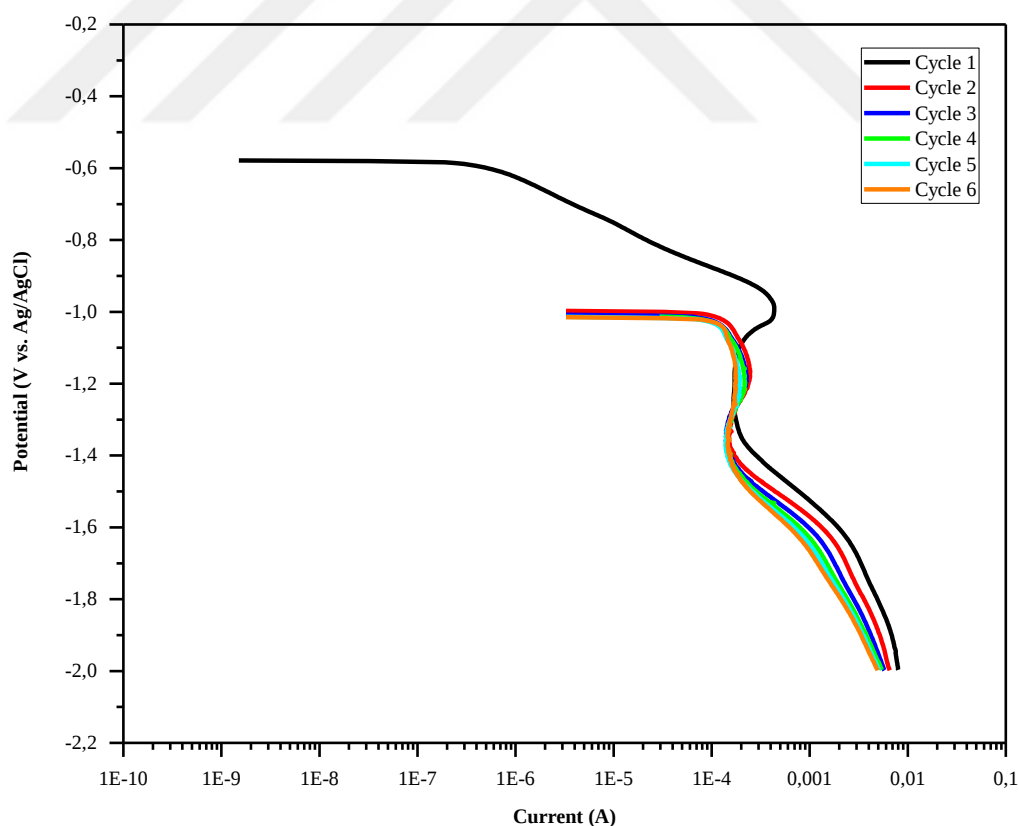


Figure 5.8 : Polarization curves of the pure tin catalyst in H_2SO_4 added 0.1 M KOH electrolyte with pH 6.8 taken from OCP to -2 V vs. Ag/AgCl.

The polarization curve given in Figure 5.8 proves that the reduction of tin oxide after the first cycle is not related to pH, because the pH of electrolytes used in CO₂ saturated 0.1 M KHCO₃ electrolyte given in Figure 5.7 and H₂SO₄ added 0.1 M KOH electrolyte given in Figure 5.8 was the same and 6.8. While the oxide is substantially reduced in the presence of CO₂ gas in CO₂ saturated 0.1 M KHCO₃, when there is no CO₂ in the electrolyte oxide is preserved as can be seen in H₂SO₄ added 0.1 M KOH electrolyte given in Figure 5.8.

In Figure 5.9, the polarization curves of the first two cycles in three different electrolytes Ar-saturated 0.1 M KHCO₃ with pH 8.5, CO₂ saturated 0.1 M KHCO₃ with pH 6.8, and H₂SO₄ acid added 0.1 M KOH with pH 6.8 are overlaid.

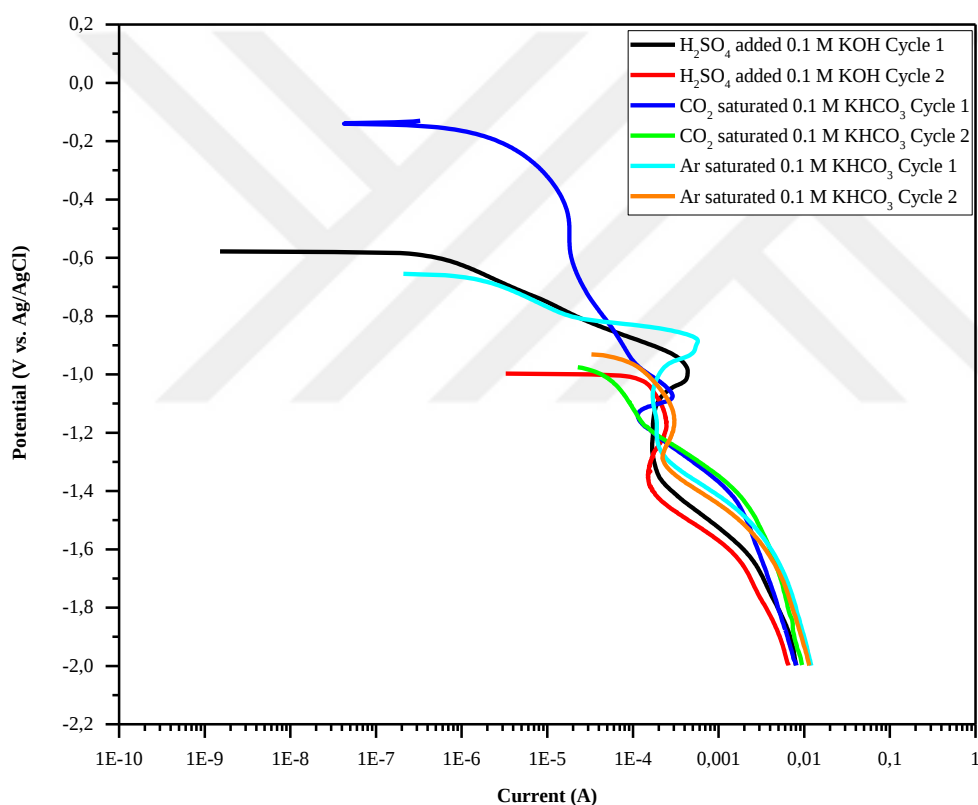


Figure 5.9 : The first two cycles of the polarization curves of pure Sn catalysts in Ar saturated 0.1 M KHCO₃, CO₂ saturated 0.1 M KHCO₃, and H₂SO₄ added 0.1 M KOH.

The similarity of the polarization curves between the Ar-saturated 0.1M KHCO₃ and H₂SO₄ added 0.1 M KOH is clear. In fact, the difference between the oxide reduction peak currents between the first and second cycle is 188 μ A for H₂SO₄ added 0.1 M KOH and 268 μ A for Ar-saturated 0.1 M KHCO₃, meaning that the oxide of pure tin electrolyte is reduced more than the one in H₂SO₄ added KOH. This could be attributed to the fact that in addition to CO₂ in the gas phase, HCO₃⁻ ions in the electrolyte can

be reduced [52]. Eventually, the reduction of both of them contributes the tin oxide reduction. Another point is that the region that HER and ECR became limited approximately at more cathodic potentials than -1.6 V vs. Ag/AgCl. The slope is steeper in CO₂ saturated 0.1 M KHCO₃, Ar saturated 0.1M KHCO₃, and H₂SO₄ added 0.1 M KOH electrolyte respectively. This shows that ECR becomes mass transport limited more than HER.

5.4.2 Polarization curves with prior constant potential electrolysis

The second polarization study was done after the 15 minutes electrolysis at -1.8 V vs. Ag/AgCl. Since in the previous polarization study the potentials are scanned with the scan rate of 5 mV/sec, there might be not enough time for the complete reduction of the tin oxide layer. To investigate the effects of longer time polarizations these sets of experiments are designed. Additionally, to prevent the re-oxidation the polarizations were started from the -1 V vs. Ag/AgCl, not OCP.

First of all, in Figure 5.10 the polarization curve obtained in the Ar saturated 0.1 M KHCO₃ electrolyte with prior constant potential electrolysis is given. The oxide reduction peak was still present and the maximum current was 316.4 μ A at -1.29 V vs. Ag/AgCl. After the first cycle, the following cycle is reduced a little more to the -1.24 V vs. Ag/AgCl and 257.8 μ A.

In Figure 5.11, polarization curves of pure tin catalyst in CO₂ saturated 0.1 M KHCO₃ electrolyte after 15 minutes constant potential electrolysis at -1.8 V vs. Ag/AgCl is given. It can be seen that the oxide peak completely disappears in the presence of CO₂ favors tin oxide reduction. Additionally, the reaction becomes mass transport limited prominently after the -1.7 V vs. Ag/AgCl.

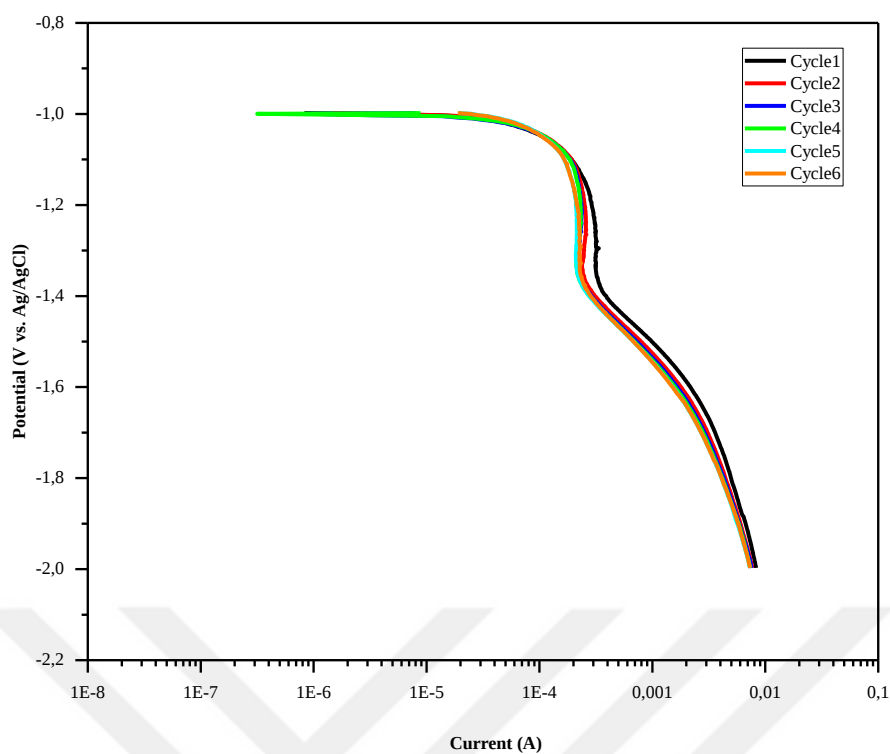


Figure 5.10 : Polarization curves of the pure Sn after 15 minutes electrolysis at -1.8 V vs. Ag/AgCl in Ar saturated 0.1 M KHCO_3 electrolyte with pH 8.5 from -1 V to -2 V vs. Ag/AgCl.

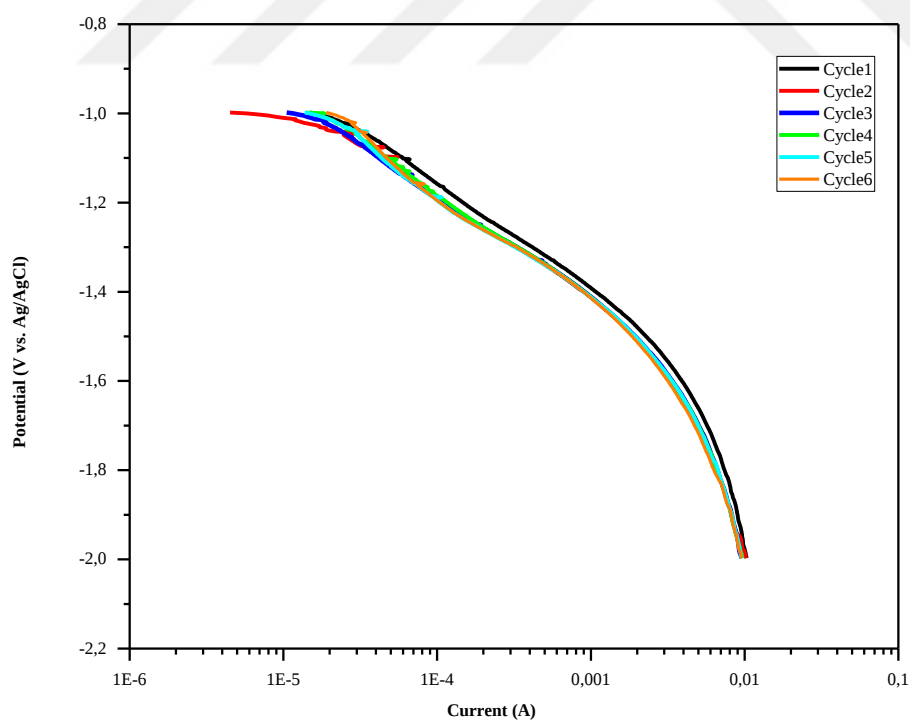


Figure 5.11 : Polarization curves of the pure tin catalyst after 15 minutes constant potential electrolysis at -1.8 V vs. Ag/AgCl in CO_2 saturated 0.1 M KHCO_3 electrolyte with pH 6.8 from -1 V to -2 V vs. Ag/AgCl.

The third experiment involved the polarization of pure tin electrode that reduced beforehand by applying a constant potential of -1.8 V vs. Ag/AgCl for 15 minutes from -1 V to -2 V vs. Ag/AgCl and given in Figure 5.12. Consistent with the previous results, the oxide layer on the tin is survived in the polarization curves of the pure tin catalyst after 15 minutes constant potential electrolysis at -1.8 V vs. Ag/AgCl in H₂SO₄ added 0.1 M KOH electrolyte and it was more similar to Ar saturated 0.1 M KHCO₃ electrolyte with pH 8.5. Similar to the polarization experiments without prior constant potential electrolysis given in Section 5.4.1, the difference between the currents passed during the tin oxide reduction peak is 18 μ A for H₂SO₄ added 0.1 M KOH and 60 μ A for Ar-saturated 0.1 M KHCO₃, which means that the oxide layer on the tin is reduced more in Ar-saturated 0.1 M KHCO₃ than in H₂SO₄ added KOH. This result designates the reduction of HCO₃⁻ ions in the electrolyte [52]. Also, the diffusion-controlled region at potentials more cathodic than -1.6 V vs. Ag/AgCl is less steep in the absence of CO₂, due to the elimination of the kinetic limitation of ECR reduction.

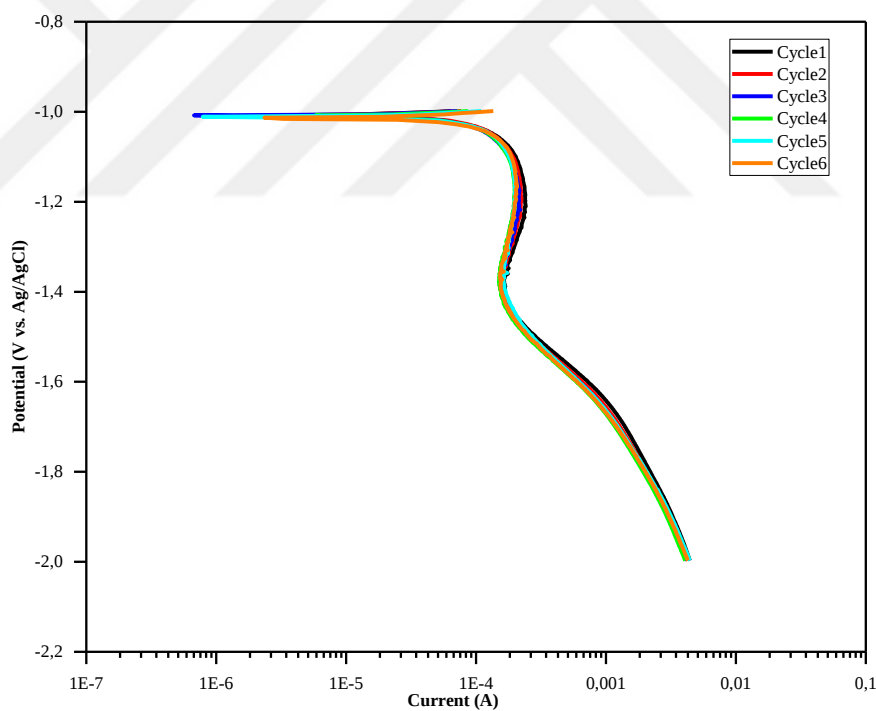


Figure 5.12 : Polarization curves of the pure tin catalyst after 15 minutes constant potential electrolysis at -1.8 V vs. Ag/AgCl in H₂SO₄ added 0.1 M KOH electrolyte with pH 6.8 from -1 V to -2 V vs. Ag/AgCl.

To compare all of the electrolytes, the first two polarization curves in Ar-saturated 0.1 M KHCO₃, CO₂ saturated 0.1 M KHCO₃, and H₂SO₄ added 0.1 M KOH are overlaid in Figure 5.13. The mass transport limited parts of the curves become steeper as the

CO₂ reduction reaction amount is higher. From highest the lowest the steepness is ordered as CO₂ saturated 0.1 M KHCO₃, Ar saturated 0.1 M KHCO₃, and H₂SO₄ added 0.1 M KOH in which there is no CO₂ reduction reaction.

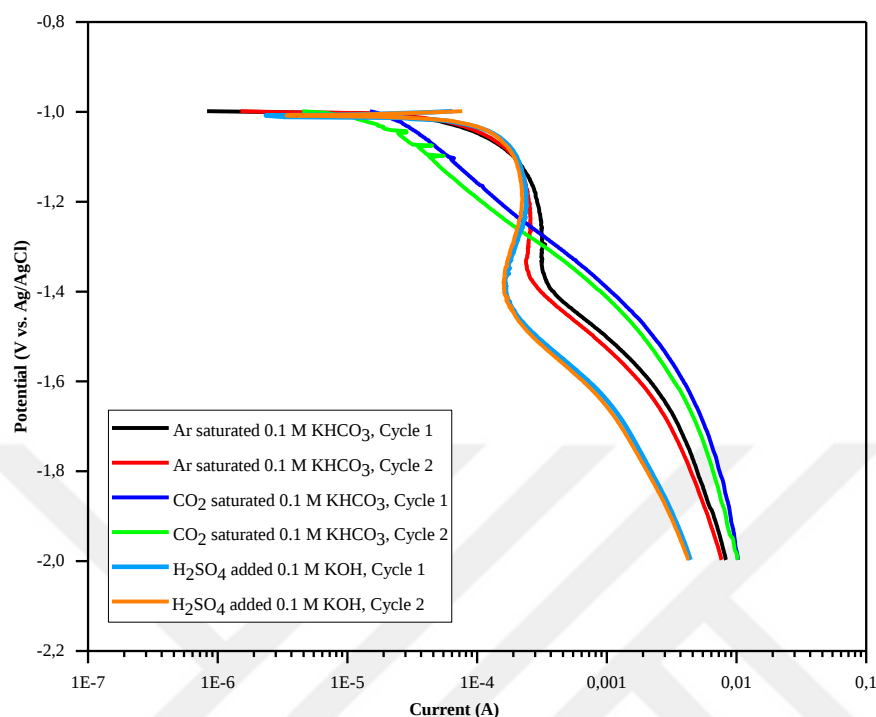


Figure 5.13 : The first two cycles of the polarization curves of pure tin catalysts in Ar saturated 0.1 M KHCO₃, CO₂ saturated 0.1 M KHCO₃, and H₂SO₄ added 0.1 M KOH after 15 minutes constant potential electrolysis at -1.8 V vs. Ag/AgCl.

As a result, with these sets of experiments, the effect of the CO₂ gas, bicarbonate, and pH on the behavior of pure tin electrode is investigated. The polarization curves showed that the tin oxide is more prone to be reduced in the presence of CO₂ gas regardless of pH. The other outcome is that the pure tin electrodes in Ar saturated 0.1M KHCO₃ electrolyte is reduced more than the ones in H₂SO₄ added 0.1 M KOH electrolyte. This could be attributed to the fact that the ECR can occur through the bicarbonate ions in the KHCO₃ electrolyte [52]. This relation between the reduction of tin oxide and the ECR reaction can be interpreted as the ECR reaction is proceeding synergetically with the tin oxide reduction reaction. However, if the ECR reaction is the reason for the tin oxide reduction or if the tin oxide reduction favors the ECR reaction is unknown. In another word, the enhanced ECR activity on the tin oxide rather than the metallic tin might be because of that the tin oxide has the optimal binding energy with the key intermediates for producing formate, or the reduction reaction of tin might be helpful for ECR reaction by providing electrons or compounds.

6. CONCLUSION

In this study, we point out the missing points in the literature about the importance of the reliable setups used in ECR experiments and a very limited amount of mechanistic studies on tin electrodes.

According to the reliable setup building studies, the annealed samples at 150, 180, and 200°C for 5 hours showed that the annealing has no significant effect on selectivity for this setup. On the other hand, by reducing the electrode area from 4 cm² to 2 cm², the reproducibility was achieved. Thus, easier charge transfer and more uniform charge distribution caused by the higher counter electrode to working electrode area ratio and the more similar sizes of the electrode and membrane, was the key factor governing the reproducibility.

Secondly, the time-dependent formate production rate is investigated on the tin electrode. The results showed that the produced formate amount at the first 10 minutes was almost 4 times higher than the remaining time intervals. As a result, when oxide layer is present on Sn, the formate production rate is higher because the tin oxide was reduced at the beginning of the experiment by the applied potential of -1.8 V vs. Ag/AgCl. The formate production rate is reduced when the tin oxide is reduced after the first 10 minutes.

The results of polarization studies showed that, the oxide on the tin electrode was reduced easier in the CO₂ saturated 0.1 M KHCO₃ (pH=6.8) compared the Ar saturated 0.1 M KHCO₃ (pH=8.5) and H₂SO₄ added 0.1 M KOH (pH=6.8). Thus, the reason for the reduction of tin oxide is not only dependent on the pH, CO₂ reduction reaction also contributes to this reaction..

In addition, the tin oxide is reduced with a higher rate in Ar saturated 0.1 M KHCO₃ than the H₂SO₄ added 0.1 M KOH. This result indicated that the reduction of HCO₃⁻ ions in the electrolyte also contributes to the tin oxide reduction.

The slopes of the polarization curves at potentials more cathodic than -1.6 V vs. Ag/AgCl ascended as follows: H₂SO₄ added 0.1 M KOH > Ar saturated 0.1 M KHCO₃, > CO₂ saturated 0.1 M KHCO₃ electrolyte. This indicates that after -1.6 V vs.

Ag/AgCl both of the HER and ECR reactions became kinetically limited. However, since the steepness is increasing with the increased CO_2 and HCO_3^- amount, the ECR reaction becomes more limited at the potentials more cathodic than the -1.6 V vs. Ag/AgCl.

In conclusion, this study reveals that there is a strong relationship between the tin oxide reduction reaction and ECR reaction. The problems identified in this study for the first time in the literature that the reason for the tin oxide is more prone to reduce while ECR reaction present, and the faradaic efficiency for formate drops significantly after the beginning of the ECR experiment due to the reduction of tin oxide. Although some studies suggest applying a bias to reform oxide on the surface, they did not reveal or mention anything about the degradation of faradaic efficiency for formate after the beginning of the experiment [9]. We identify these problems that were not mentioned in the literature before, and the reasons of them with this study.

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