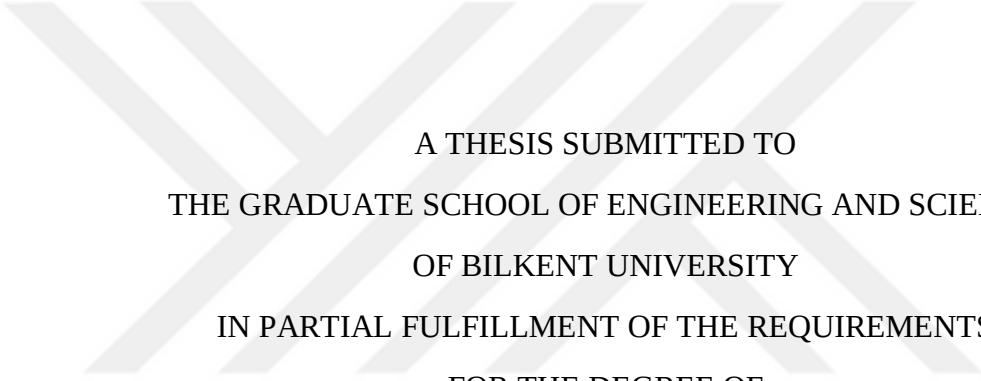


**FABRICATION, CHARACTERIZATION, AND ELECTROLYSIS OF  
MESOPOROUS CALCIUM IRON OXIDE  $\text{CaFe}_2\text{O}_4$  THIN FILM ELECTRODES**



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By  
Hamid Ali Raza  
June, 2023

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By Hamid Ali Raza

June, 2023

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

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## ABSTRACT

### FABRICATION, CHARACTERIZATION, AND ELECTROLYSIS OF MESOPOROUS CALCIUM IRON OXIDE ( $\text{CaFe}_2\text{O}_4$ ) THIN FILM ELECTRODES

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M.Sc. in Chemistry

Advisor : Ömer Dağ

June, 2023

Transition metal ferrites have attracted the attention of many scientists because of their low cost, high earth abundance, low band gap, and biocompatibility. They can be prepared in different morphologies, and because of this, they may have a high surface area and excellent electrochemical and photoelectrochemical properties. In this thesis, we have prepared mesoporous calcium iron oxide (CFO) thin films using the molten-salt assisted self assembly (MASA) method and analyzed its electrochemical applications for oxygen evolution reaction (OER). The clear and homogeneous aqueous solution of metal salts (Calcium nitrate tetrahydrate, iron (III) nitrate nonahydrate) and surfactants (cetyltrimethyl ammonium bromide, CTAB, and  $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$ ,  $\text{C}_{12}\text{EO}_{10}$ ) were coated on microscope glass slides by various coating techniques to obtain mesophases. Later on, the mesophases and their aging process were analyzed by the small-angle XRD measurements, ATR-FTIR and POM. Diffraction lines between  $1$  and  $5^\circ$ ,  $2\theta$ , indicate the formation of ordered lyotropic liquid crystalline mesophases. These mesophases were subjected to calcination at various temperatures, and the powders obtained were further characterized by wide-angle XRD measurements, SEM, EDX, TEM, XPS, ATR-FTIR, and  $\text{N}_2$ -adsorption and desorption techniques. The calcium iron oxide in highly crystalline form are prepared at  $800^\circ\text{C}$ , having thin film morphology. Interestingly, we are able to retain the porous structure even at such a high temperature. The amorphous phase contains calcium carbonate as a side product that was confirmed by ATR-FTIR, XRD and XPS

data. The maximum surface area of mesoporous material is 145 m<sup>2</sup>/g, while water being used as a solvent.

Similarly, we prepared the same materials using different precursors (chlorides) and solvent (ethanol) to see the effect of counter anion and solvent on the porosity, self-assembly, morphology, and electrocatalytic performance of the material in the OER. We observed that while using chloride precursors, the material was quite crystalline even at low calcination temperature, i.e., 300 °C. Iron oxide forms at low temperatures and with the increase in temperature, it finally transforms to calcium iron oxide. But in this case, the materials are not as porous and display a surface area of only 5 m<sup>2</sup>/g at 300 °C. Similarly, we also characterized these materials using the above-mentioned techniques.

While using ethanol as a solvent, keeping nitrate precursors the same, and using two different mole ratios of calcium and iron (2:4, 3:6), we also tried to elucidate the effect of solvent on morphology and catalytic properties of materials. In this case, we observed that the surface area did not drop immediately (as in the case of water) but gradually. The maximum surface area, obtained are almost similar to the material prepared by water as a solvent.

All the solutions mentioned above (prepared by using different precursors, solvent, and mole ratios) are coated (by dip-coating) on the graphite rod to determine the catalytic activities by various electrochemical experiments (cyclic Voltammetry (CV), chronopotentiometry (CP), and chronoamperometry (CA)). Electrodes are quite stable in all cases, even in harsh conditions (CP at 100 mA for 2 h). Also, enhanced activity may be because of reduced resistance and increased conductivity with the usage. In all cases, the minimum Tafel slopes are almost similar, and vary between 47 and 83 mV/dec. The overpotentials at various current densities are 260 mV for 1 mA/cm<sup>2</sup>, about 450 mV for 10 mA/cm<sup>2</sup>, and about 700 mV for 100 mA/cm<sup>2</sup>.

Additionally, effect of the coated material's thickness on the electrocatalyst's activity is also investigated. It has been found that by decreasing the amount of coated material (by diluting up to 100 times), there is no change in the activity of the material. Finally, our

results indicate that these types of energy material's (CFO) performance depends on the surface's characteristics rather than the coating material's thickness or the pores' size. Also, we found it unnecessary to waste a large amount of metal salts to fabricate these materials; OER performance is similar regardless of coating thickness. Therefore, the surface reaction is the primary factor in electrode activity, with pore shape being the critical characteristic.

Keywords: Molten-salt assisted self-assembly, calcium ferrite, lyotropic liquid crystalline mesophase, oxygen evolution reaction, mesoporous thin film.

## ÖZET

### ÜRETİM, KARAKTERİZASYON VE MEZOPENÖR ELEKTROLİZİ KALSIYUM DEMİR OKSİT ( $\text{CaFe}_2\text{O}_4$ ) İNCE FİLM ELEKTROTLAR

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Geçiş metali ferritler, düşük maliyetleri, yeraltı kaynaklarının yüksekliği, düşük bant aralığı ve biyolojik uyumluluğu nedeniyle ilgi çekmiştir. Farklı morfolojilerde hazırlanabilmelerinden, yüksek yüzey alanına, mükemmel elektrokimyasal ve foto-elektrokimyasal özelliklere sahip olabilirler. Bu tezde, eriyik tuz destekli kendi kendine oluşma (MASA) yöntemi kullanılarak aragözenekli kalsiyum demir oksit (CFO) ince filmleri hazırlandı ve oksijen evrim tepkimesi (OER) için elektrokimyasal uygulamalarını analiz edildi. Metal tuzları (kalsiyum nitrat tetrahidrat, demir(III) nitrat nonahidrat) ve yüzey aktif maddelerin (setil amonyum bromür, CTAB ve  $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$ ,  $\text{C}_{12}\text{EO}_{10}$ ) homojen sulu çözeltileri hazırlandı ve çeşitli kaplama teknikleriyle mikroskop cam slaytlar üzerine kaplandı ve arafazları elde edildi. Daha sonra, arafazlar ve yaşlanma süreçleri küçük açılı XRD ölçümleri, ATR-FTIR spektroskopisi ve POM görüntüleme teknikleri kullanılarak analiz edildi. 1 ile 5°, 2θ arasındaki kırınım çizgileri, düzenli lityotropik sıvı kristal arafazların oluşumunu göstermektedir. Bu arafazlar çeşitli sıcaklıklarda kalsinasyona tabi tutuldu ve elde edilen tozlar geniş açı XRD ölçümleri, SEM, EDX, TEM, XPS, ATR-FTIR ve  $\text{N}_2$ -adsorpsiyon ve desorpsiyon gaz analizör teknikleriyle karakterize edildi. Kalsiyum demir oksidi, 800 °C'de ince film morfolojisine sahip olarak yüksek kristal yapıda hazırlandı. İlginç bir şekilde, gözenekli yapıyı bu kadar yüksek bir sıcaklıkta bile koruyabildik. Amorf faz, ATR-FTIR spektroskopisi ile doğrulanan kalsiyum karbonat ve demir oksit içeren yan ürün olan yapı daha sonra XRD ve XPS verileriyle doğrulandı. Çözücü olarak su

kullanılarak elde ettiğimiz mezogözenekli malzemenin maksimum yüzey alanı  $145 \text{ m}^2/\text{g}$  olarak belirlendi.

Benzer şekilde, farklı girdiler (klorürler) ve çözücüler kullanarak aynı malzemeler hazırlandı ve karşı iyonun ve çözücünün malzemenin gözeneklilik, kendi kendine oluşma, morfoloji ve elektrokatalitik performansı üzerindeki etkileri gösterildi. Klorür girdileri kullanıldığında, malzemenin daha düşük kalsinasyon sıcaklığında bile oldukça kristalin demir oksit oluştuğu gözlemlendi. Daha sonra, sıcaklık arttıkça karışımın kalsiyum demir okside dönüştüğü belirlendi. Ancak, bu durumda malzemelerin gözenekliliğinin azaldığı ve  $300 \text{ }^\circ\text{C}$ 'de sadece  $5 \text{ m}^2/\text{g}$  yüzey alanına sahip olduğu belirlendi. Benzer şekilde, bu malzemeler de yukarıda bahsedilen teknikler kullanılarak karakterize edildi.

Nitrat girdilerini aynı tutarak ve iki farklı kalsiyum ve demir (2:4, 3:6) mol oranlarında etanolün çözücü olarak kullanıldığı çözeltiler hazırlandı ve çözücünün morfoloji ve katalitik özelliklere etkisi gösterildi. Bu durumda, yüzey alanının hemen düşmediğini (suyun durumunda olduğu gibi), ancak kademeli olarak azaldığını gözlemledik. Elde edilen maksimum yüzey alanları, suyun çözücü olarak kullanıldığı malzemelere benzediği görüldü.

Yukarıda bahsedilen farklı girdiler, çözücü ve mol oranları kullanılarak tüm çözeltileri grafit çubuk üzerine daldırma-çekme kaplama yöntemiyle kaplandı ve çeşitli elektrokimyasal deneyler (siklik voltametri (CV), kronopotansiyometri (CP) ve kronoamperometri (CA)) ile katalitik aktiviteleri belirlendi. Elektrotlar, tüm durumlarda, hatta zorlu koşullarda (2 saat boyunca  $100 \text{ mA}/\text{cm}^2$  de CP) oldukça kararlıdır. Ayrıca, uzun süre kullanım ile direncin azalması ve iletkenliğin artması nedeniyle artan aktivite gözlemlendi. Tüm durumlarda, minimum Tafel eğimi değerleri  $47\text{-}83 \text{ mV}/\text{dec}$  olarak belirlendi. Çeşitli akım yoğunluklarında gerekli potansiyelin, sırasıyla  $1 \text{ mA}/\text{cm}^2$  için  $260 \text{ mV}$ ,  $10 \text{ mA}/\text{cm}^2$  için yaklaşık  $450 \text{ mV}$  ve  $100 \text{ mA}/\text{cm}^2$  için yaklaşık  $700 \text{ mV}$  olduğu belirlendi.

Ayrıca, kaplanmış malzemenin kalınlığının elektrokatalizörün aktivitesi üzerindeki etkisi aydınlatıldı. Kaplanan malzeme miktarını azaltıldığında (100 kat seyrelterek) malzemenin

aktivitesinde herhangi bir deęişiklik olmadığı gözlemlendi. Sonuçlarımız, bu tür enerji malzemelerinin (CFO) performansının kaplama malzemesinin kalınlığı veya gözeneklerin boyutu yerine yüzeyin özelliklerine baęlı olduğunu gösterdi. Ayrıca, bu malzemeleri üretmek için büyük miktarda metal tuzunu israf etmenin gereksiz olduğunu bulduk, çünkü kaplama kalınlığına bakılmaksızın performansın benzer olduğunu belirledik. Bu nedenle, yüzey reaksiyonu, yüzey morfolojisi gibi özellikler, elektrot aktivitesinde temel faktörlerdir.

**Anahtar kelimeler:** Eriyil tuz destekli kendi-kendine oluşma, kalsiyum ferrit, lityotropik sıvı kristal arafaz, oksijen evrim reaksiyonu, mezogözenekli ince film.

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## **List of Abbreviations**

LC : Liquid Crystal

LLC : Lyotropic Liquid Crystal

LLCM : Lyotropic Liquid Crystal Mesophase

HTM : Hard Templating Method

STM : Soft Templating Method

CMC : Critical Micellar Concentration

EISA : Evaporation Induced Self Assembly

CTAB : Cetyltrimethylammonium Bromide

MASA : Molten salt Assisted Self Assembly

SCE : Soft Confinement Effect

POM : Polarized Optical Microscopy

ATR-FTIR : Attenuated Total Reflection Fourier-Transform Infrared

XRD : X-Ray Diffraction

PXRD : Powder – X-Ray Diffraction

FWHM : Full Width Half Maxima

SEM : Scanning Electron Microscopy

EDX : Energy Dispersive X-Ray Spectroscopy

TEM : Transmission Electron Microscopy

CFO : Calcium Iron Oxide

XPS : X-Ray Photoelectron Spectroscopy

BET : Brunauer, Emmett and Teller

BJH : Barrett-Joyner-Halenda

OER: Oxygen Evolution Reaction

WE : Working Electrode

RE : Reference Electrode

CE : Counter Electrode

FTO : Fluorine Doped Tin Oxide

NHE : Normal Hydrogen Electrode

SCE : Standard Calomel Electrode

CV : Cyclic Voltammetry

CA : Chronoamperometry

m-CA : Multi-step Chronoamperometry

CP : Chronopotentiometry

m-CP : Multi-step Chronopotentiometry

# Chapter 1

## 1. Introduction

### 1.1. Mesoporous Materials and Metal Oxides:

Mesoporous materials got the attention of many researchers because of their unique properties, such as high surface area, narrow pore size distribution, high porosity, biocompatibility, and low toxicity. They have several applications in various fields, especially in catalysis, drug delivery systems, batteries, green energy, and energy storage[1][2]. The first family of mesoporous materials prepared by LC templating approach was discovered by Kresge et al., called as M41S family [3]. MCM-41 is a member of this family, having a hexagonal arrangement of pores. They reported the formation of these materials using the LC templating mechanism. The mesostructured material forms by self-assembling polymerizing inorganics with micelles of surfactants. The surfactant used in this synthesis was cationic (cetyltrimethylammonium bromide, CTAB). The pore size was proposed to vary with the surfactant's alkyl chain length [3]. The other members of the M41S family have a cubic phase (MCM-48) [4].

Since the discovery of mesoporous materials in 1992, many researchers have contributed to this field to understand the mechanism of their formation, characterization, and applications of these highly ordered silicates [5][6] Ulrike et al., in their review, stated that up to that time, there was not much work on the application of these superior materials. She explained that there is no need for narrow pore size distribution and ordered pores; the only requirement is a high surface area. Also, note that transition metal oxides

other than silica are the most important materials which can be synthesized by this method and are not accessible by any other methods [5].

It is also important to mention that in 1990, Kato and co-workers prepared trimethylammonium-kanemite complexes by the surfactant-directed arrangement of 3D SiO<sub>2</sub> networks. The material prepared had a surface area of 900 m<sup>2</sup>/g and a 2-4 nm pore diameter, typical for mesoporous materials. Also, they claimed that pore size varies with the chain length of the surfactant used [6].

The first mesoporous silica materials using non-ionic surfactants were reported by Pinnavaia et al. in 1995. This synthesis was based on self-assembly between neutral inorganic precursors and neutral amine micelles and hydrogen-bonding interactions [7]. The same group also reported the materials' synthesis using an electrostatic templating approach. It revealed that the material prepared by this method has thicker pore walls than the material designed by the neutral surfactant. It was also demonstrated that neutral templating pathways produce small domain sizes, thicker pore walls, and improved textural properties [8].

Schüth and co-workers synthesized many mesoporous metal oxides using charged surfactants under ambient pH conditions. The same group also reported the synthesis of various mesoporous metal oxides, phosphates, and sulfides using different combinations of surfactants and inorganic precursors. By controlling interface condensation processes, metal oxides have also been synthesized [5], [9], [10]. Huo et al. presented a model for the morphologies of silicate-surfactant mesophases, which also explained the transformation of the lamellar and hexagonal phases at different conditions. They claimed that it could also be applied to non-silicate surfactant-based systems [11].

The first example of mesoporous metal oxide, titania (TiO<sub>2</sub>), having open pores even after calcination was reported by Ying and co-workers in 1995 [12]. Göltner et al. reported the synthesis of mesoporous silica, but this time large amount of surfactant was used as compared to M41S [13]. Later, evaporation-induced self-assembly and nano-casting enhanced the work pace on synthesizing mesoporous metal oxides. The ordered metal oxide synthesis usually employs a hard templating (HT) approach, in which already

prepared mesoporous silicates or carbons are used as a template. The details of these methods are given in the following sections [14] [15].

#### 1.1.1. Synthesis of Mesoporous Metal Oxides Using Hard Template (HT) Method:

The hard templating method is also known as the nano-casting or exo-template method. This method uses solid materials such as mesoporous silica or carbon as templates to prepare mesoporous metal oxides. The template is mixed with inorganic precursors that fill the voids of the template, and after converting the precursor into its oxide by calcination, the template is removed by chemical etching or calcination [16][17]. This method is versatile for the synthesis of those metal oxide materials which are not easy to prepare using the soft template method (STM). Highly porous solids can be prepared using porous carbon or silica as hard templates, which may find many applications. The schematic representation of the hard templating method is shown in Figure 1.1:



**Figure 1. 1.** Schematic representation of hard templating method (HTM). Adapted with permission from license No. 5562470501392, ELSEVIER, 2013.

Mesoporous silicas are preferred for HTM because of their highly ordered structure and uniform pore size distribution. Kim et al. in 2007 reported the synthesis of mesoporous  $\text{SnO}_2$  and  $\text{SnO}_2$  nanowires as anode material in lithium-ion batteries using a mesoporous silica template. The surface area of mesoporous tin oxide was larger than tin oxide nanowires [18]. Mesoporous metal oxides such as  $\text{MgO}$ ,  $\text{CeO}_2$ ,  $\text{ZnO}$ , and  $\text{TiO}_2$  have also been synthesized extensively in the literature using carbon as a template. [19]–[24]

Later, porous carbon, i.e., CMK-3, as a hard template got attention and has been extensively used in synthesizing mesoporous metal oxide. Carbon is also a useful hard template because it is easy to remove by calcination but requires an inert atmosphere during heating. Otherwise, it can impart impurities (carbonates) to the metal oxides [25].

To remove the silica framework, HF or NaOH solutions are used to ensure silica dissolution, leaving metal oxide behind.

Additionally, Zhao et al. synthesized a variety of mesoporous metal oxides such as  $\text{Fe}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{CeO}_2$ , and  $\text{Cr}_2\text{O}_3$  using silica as a hard template. [26], [27]

### 1.1.2. Synthesis of Mesoporous Metal Oxides Using Soft Template Method:

The soft templating method (STM) is based on the use of surfactants. In this method, surfactants are dissolved in a solvent along with inorganic precursors, surfactants micelles and precursors are co-assembled to a mesostructured solid, and the surfactants are removed by calcination. The micellization occurs when surfactants are added to a proper solvent above a certain concentration (critical micellar concentration CMC). The micellization occurs due to hydrophobic and hydrophilic end groups of surfactants in the presence of an appropriate solvent. It also depends on the concentration of the surfactant used [28]. The details of this method are given in the next section. The schematic representation of this method is given below:

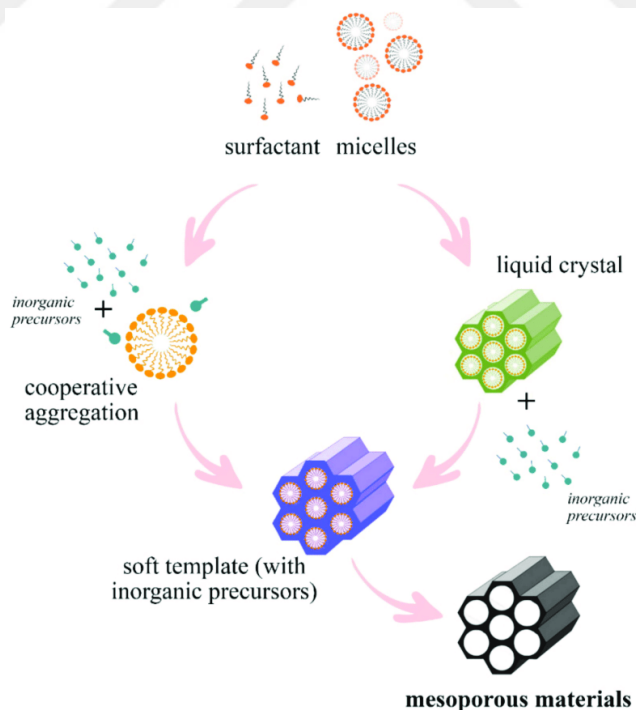


**Figure 1. 2.** Schematic representation of soft templating method (STM). (MDPI-Catalysts)

The first mesoporous material was also synthesized using the soft template method by J.S Beck et al. and Huo et al. in 1994 also reported the number of mesoporous metal oxides by soft template methods (using cationic and anionic surfactants) such as  $\text{WO}_3$  and  $\text{Fe}_2\text{O}_3$  [4]. In the 1990s, Yang et al. synthesized various metal oxides  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{WO}_3$ ;  $\text{Nb}_2\text{O}_5$  [29], [30];  $\text{ZrO}_2$  [31], [32];  $\text{HfO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{SnO}_2$ , and mixed metal oxides  $\text{SiAlO}_{3.5}$ ,  $\text{SiTiO}_4$ ,  $\text{ZrW}_2\text{O}_8$ ,  $\text{ZrTiO}_4$ ,  $\text{SiTiO}_4$ ,  $\text{Al}_2\text{TiO}_5$  and  $\text{ZrTiO}_4$  using surfactants system [33].

*Evaporation Induced Self Assembly (EISA)*, introduced by Brinker's research group, is another widely used soft template method [34]. It consists of four steps. (1) mixing of precursors, surfactants, and solvent at the same time, followed by coating (spin, dip, or spray depending on the purpose) on a substrate (2) evaporation of solvent forms a semi-solid having mesostructured material (3) hydrolysis and condensation solidifies the precursors and finally (4) a template is removed by chemical or thermal means [35]. This method requires slow evaporation to produce an ordered mesoporous material. Fast solvent evaporation may also lead to thicker pore walls, reducing the surface area [36]. To decrease the evaporation rate of solvent, non-aqueous solvents have also been employed.

## **1.2. Lyotropic Liquid crystalline Mesophases (LLC):**

A liquid crystal is a fourth phase of matter with properties between solids and liquids. They flow like liquids, have ordered structures like solids, are thermodynamically stable, and have unique mesostructures (mesophases). Reintzer first introduced liquid crystals in 1888 to the literature. Later, a German scientist Lehmann named this thermodynamically stable liquid crystalline phase [37]. There are two types of liquid crystals, thermotropic liquid crystals (TLC) and lyotropic liquid crystals (LLC). In this thesis, we will work with lyotropic liquid crystals (LLC)—surfactants that are dissolved in a solvent in high concentrations, forming LLC mesophases. The arrangement of surfactant molecules into 3D structures (mesophase) depends on the solvent used. Surfactant molecules have long hydrophobic chains with a hydrophilic head. Therefore, they form micelles at certain concentrations (critical micellization concentration, CMC) and evaporation of the excess solvent; these micelles arrange themselves to form, LLC mesophases [38]. There are some

factors that affect the structure of LLC, such as the amount of water (solvent), pH, temperature, and concentration of surfactants, which have been extensively investigated in the literature on how a change of composition affects the material morphology [39]. For example, vesicle, rod, and nanofibers shaped silica, mesoporous silica, and cylindrical-shaped silica were prepared from the micelle's solutions [33], [40].

The LLC phase has three common structure types: cubic, hexagonal, and lamellar. A polarized optical microscope can monitor these phase formations except cubic because it is an isotropic and non-birefringent phase. POM can visualize lamellar and hexagonal mesophases because they are anisotropic and birefringent (having two different refractive indices) [41]. Also, LLC mesophases can be characterized by the small-angle x-ray diffraction (XRD) measurement. Since LLCs have larger unit cells due to large micelle size, they usually diffract at small angles,  $1\text{--}5^\circ$ ,  $2\theta$ .

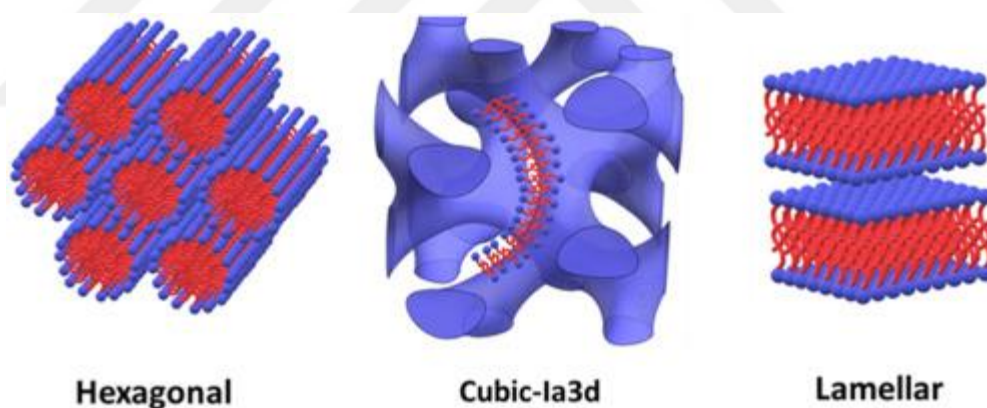


**Figure 1. 3.** Three phases of LLC (hexagonal, cubic, and lamellar). Adapted with permission from license No. 5562480092984, ELSEVIER, 2020.

Six different lyotropic liquid crystalline phases have been observed in polymers by Paschalis *et al.* and identified as cubic, hexagonal, and lamellar phases in 1997 [42]. Mesoporous metal oxides with a larger pore (up to 140 Å) were prepared using LLC mesophases by the soft-templating method. Porous niobia, silica, and titania were synthesized using a soft templating approach. The EISA method has been employed to synthesize several mesoporous metal oxides (such as  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{Al}_2\text{O}_3$ ,

SiO<sub>2</sub>, SnO<sub>2</sub>, WO<sub>3</sub>, HfO<sub>2</sub> and various mixed metal oxides (SiAlO<sub>y</sub>, Al<sub>2</sub>TiO<sub>y</sub>, ZrTiO<sub>y</sub>, SiTiO<sub>y</sub>, ZrW<sub>2</sub>O<sub>y</sub>) by Yang et al. and Tian et al. [43]–[45].

The LLC approach can also be used to prepare porous metal sulfides. Hexagonal LLC has been used to prepare mesoporous ZnS (hollow capsule-like morphology) with nanostructured walls [46]. The growth of AgBr and SnO<sub>2</sub> microwire has been shown by LLC mediated synthesis approach by using CTAB and oligo (ethylene oxides) as surfactants. Also, nanowires were electrodeposited from the reverse hexagonal LC phase, and high-density bundles of wires were produced. Kijima et al. also produced single-crystalline platinum sheets using LLCs of polyoxyethylene-type polymers and other non-ionic surfactants [47]–[49].

Lyotropic liquid crystals formed with a low metal salt concentration with excess water have been investigated to understand the role of ions in the mesophase until the discovery of a new type of LLCs that uses salts as solvent. Therefore, the mesostructured solid produced by this approach was limited, even in high surfactant concentration gels. In 2001, Dag group introduced a new type of LLC mesophase having high salt concentrations. Oligo (ethylene oxides) or pluronic-type surfactants have been employed in the new LLC phase [50]. The C<sub>12</sub>EO<sub>10</sub> (10-lauryl ether) has been investigated using different metal salt mixtures with varying mole ratios. Due to the soft confinement effect, adding excess metal salts to the new mesophase (metal salt/water/ C<sub>12</sub>EO<sub>10</sub>) is possible. The effect of anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and ClO<sub>4</sub><sup>-</sup>) on the hydrophilicity of surfactant was investigated, and they concluded that the structure and stability of the lyotropic liquid phase could be related to the hydrophilicity of non-ionic surfactant and ion density. As nitrate tends to interact with the metal ion, which decreases the ion density, there is more tendency to uptake more nitrate salt [51]. Dag et al. also reported that salt uptake could be extensively increased using charged surfactant along with non-ionic surfactant C<sub>12</sub>EO<sub>10</sub>. Zinc nitrate [Zn (H<sub>2</sub>O)<sub>6</sub>] (NO<sub>3</sub>)<sub>2</sub> was used along with C<sub>12</sub>EO<sub>10</sub>-CTAB (CTAB is cetyltrimethylammonium bromide) or C<sub>12</sub>EO<sub>10</sub>-SDS (sodium dodecyl sulphate) couples to ensure that high salt concentrations of metal salt were incorporated with a minimal amount of water that prevents salt crystallization [52]. In addition, metal sulfide films were also produced using pluronic (P85) copolymer as a non-ionic surfactant along with

CTAB [53]. In 2012, the same group replaced transition metal salts with lithium salts to produce lithium ion-rich LLC mesophases that have been employed as gel electrolytes in electrochemical applications. It also demonstrated that further salt uptake could be enhanced along with transition metal salts. [54]

### **1.3. Molten Salt-Assisted Self-Assembly (MASA) Approach:**

Dag group later introduced a facile synthesis method, molten salt-assisted self-assembly (MASA), to synthesize mesoporous materials. This method uses salt, solvent, and surfactant (each of the two); one solvent (water or ethanol) is necessary to obtain a homogeneous solution and for spin-coating or drop-casting to prepare mesoporous metal oxide thin films, and the molten salt behaves like a second solvent in the assembly process, which is the reason for salt-surfactant LLC self-assembly. As a result of the soft confinement effect (SCE), salt never crystallizes even at low temperatures (such as liquid nitrogen temperature) in the hydrophilic domains of mesophase (in confined spaces). One can confine more salt in the LLC mesophases by coupling the charged surfactant (CTAB) non-ionic surfactant with a non-ionic surfactant. The interaction between molten salt domains and charged hydrophilic-hydrophobic interface of surfactant domains in the LLC stabilizes the salt surfactants LLC mesophases. Also, the collective assembly of both used surfactants gives the same result. Note also that the soft confinement effect (SCE) has been used to determine the pore diameter of porous materials [55], [56][57][58][59].

The literature has extensively investigated that metal ion concentration can be increased by increasing the charged surfactant concentration, stabilizing the mesophase. So, the presence of CTAB in the MASA approach is necessary to stabilize and improve the salt uptake ratio of the mesophase. Also, the collective assembly of both used surfactants gives the same result. In the assembly process, the precursor solution is spin-coated on a glass substrate to obtain LLC mesophase and then heated at high temperatures to burn the surfactants and to convert the metal salts to metal oxides; in this way, mesoporous thin films can be prepared. Evaporation-induced self-assembly (EISA) can also be used to prepare mesoporous materials as it is a facile, efficient, and quick method to prepare

uniform thin films [35][60]. Still, it has some limitations as salt uptake concentration is limited in this method, and evaporation of solvent immediately gives a mesostructured solid. Hence, EISA is more appropriate for metal alkoxides precursors that undergo the stages of condensation and hydrolysis. The polymerized species, such as metal hydroxides, oxyhydroxides, and surfactants, go through a self-assembly process and form a solid or semi-solid mesostructured material. In the MASA approach, stable LLC mesophases are obtained, which further go through some steps to yield mesoporous materials with high surface area. Also, it is not restricted to metal alkoxides. The surfactants are mixed into a solvent, i.e., water or ethanol (in this thesis), to obtain a clear solution, and then salts are added to obtain a homogeneous solution. The solution can be coated on a glass substrate by various techniques, such as dip coating, spin coating, and spray coating, depending on the purpose (monoliths, thin films, or powders).

The MASA approach was introduced in 2011 and extensively used to synthesize mesoporous materials. First, Zinc oxide (ZnO) and Cadmium oxide (CdO) coated silica thin films were prepared to have a 1.6 nm thick metal oxide layer over the mesoporous silica internal surface. It was shown that a large amount of metal salts could be confined in the domains of surfactants and silica walls [56]. Also, highly conductive gel electrolytes from different lithium salts in water were prepared using non-ionic surfactants, which are highly useful in electrochemical applications [61], [62]. Later on, this method was also applied to the synthesis of mesoporous metal titanates such as  $\text{Zn}_2\text{TiO}_4$ ,  $\text{CdTiO}_3$ ,  $\text{CoTiO}_3$ ,  $\text{MnTiO}_3$ , and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  [55], [61], [63]. Metal lithiates ( $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiMn}_{2-x}\text{O}_{4-x}$ ) were also prepared and investigated by the MASA approach and used as electrocatalysts in water splitting at low overpotentials [64]–[66]. This method also synthesized metal cobaltites ( $\text{MnCo}_2\text{O}_4$ ,  $\text{ZnCo}_2\text{O}_4$ , and  $\text{NiCo}_2\text{O}_4$ ) as thin films [67].

Nickel oxide (NiO) was synthesized as an electrochromic material and OER electrocatalyst with a very low overpotential (200mV) at  $1\text{mA}/\text{cm}^2$  current density. Also, the conversion of NiO to nickel hydroxide with repetitive cyclic voltammetry has been shown [68]. The synthesis of mesoporous lithium metal phosphates was reported by the same group in which they synthesized  $\text{LiMPO}_4$  ( $\text{M} = \text{Mn}, \text{Co}, \text{and Ni}$ ) with a high surface of  $79\text{ m}^2/\text{g}$  and a high charge capacity of  $93\text{ mAh/g}$ , beneficial for Li-ion batteries.[69]

All of the above-mentioned materials were prepared by using two non-ionic surfactants, mostly P123 and 10-lauryl ether but can be extended to other non-ionic surfactants. This thesis used 10-lauryl ether and CTAB as non-ionic and charged surfactants, respectively, and the MASA approach to synthesize mesoporous calcium iron oxide thin films.

#### 1.4. Structure of Calcium Iron Oxide (CFO):

In the early 90s, the crystal structure of  $\text{CaFe}_2\text{O}_4$  (CFO) was determined from single crystal studies. It was found that the CFO has an orthorhombic system with unit cell parameters of  $a = 9.230$ ,  $b = 10.070$ , and  $c = 3.024 \text{ \AA}$ . According to the data above, oxygen is coordinated with iron (Fe) in a distorted octahedron manner, while the nine oxygen atoms coordinate with calcium ions ( $\text{Ca}^{2+}$ ). This type of coordination was also seen in  $\text{CaTi}_2\text{O}_4$  and  $\text{CaV}_2\text{O}_4$ , which are isomorphic with  $\text{CaFe}_2\text{O}_4$ .

In the structure of CFO, two Fe atoms are not equivalent, and oxygen atoms octahedrally surround them. As mentioned, the  $\text{Ca}^{2+}$  ion is surrounded by 8 or 9 oxygen atoms, six oxygen atoms form a trigonal prism with an axis parallel to  $c$ , and two oxygen atoms are on the same level as calcium in a staggered bond position (Bunn, 1945). The ferrites with formula  $\text{MFe}_2\text{O}_4$  have spinal structure except for  $\text{CaFe}_2\text{O}_4$  because  $\text{Ca}^{2+}$  tends to coordinate in an eight or 9-fold manner [70][71].

The structure of calcium ferrite is given in Figure 1.4.

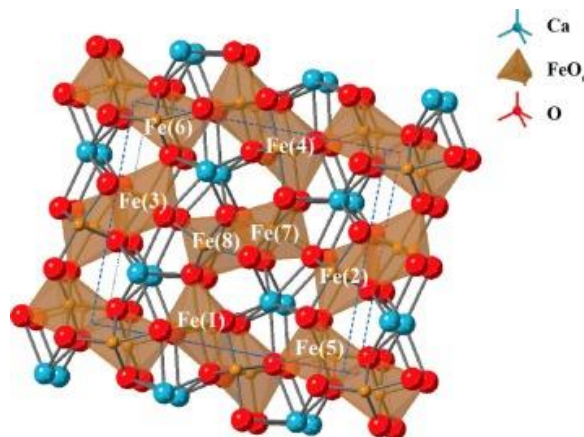


**Figure 1. 4.** Elementary cell of  $\text{CaFe}_2\text{O}_4$ . Adapted with permission from license No. 5562481037916, ELSEVIER, 2018.

## 1.5. Synthesis of Calcium Ferrite Nanomaterials and their Applications:

Transition metal ferrites have attracted the attention of many scientists because of their low cost, high earth abundance, low band gap, and biocompatibility. They can be prepared in different morphologies, and because of this, they have a high surface area and excellent electrochemical and photoelectrochemical properties.

Calcium iron oxide is more advantageous because of its biocompatibility and eco-friendly nature due to the presence of  $\text{Ca}^{2+}$  instead of other heavy metals. Because of its desirable properties,  $\text{CaFe}_2\text{O}_4$  has been employed in high-temperature sensors, lithium-ion batteries as a photocathode, targeted drug delivery, gas absorbers, and other applications. Sulaiman. et al. synthesized  $\text{CaFe}_2\text{O}_4$  orthorhombic nanoparticles by auto-combustion and co-precipitation methods and showed that nanoparticles prepared by co-precipitation have uniform size distribution and excellent magnetic properties [72]. Damerio. et al. prepared thin films of calcium iron oxide on  $\text{TiO}_2$  by solid-state synthesis method with a thickness of around 100 nm and studied their magnetic properties by SQUID magnetometry and Mössbauer spectrometry[73]. Another work for synthesizing  $\text{CaFe}_2\text{O}_4$  nanoparticles with cubic spinel, orthorhombic, or mixed phase structures using a facile sol-gel method and the appropriate heat treatment by Das. et al.[74] Candeia. et al. have used the polymeric precursor method to synthesize spinal pigment  $\text{CaFe}_2\text{O}_4$ , which has a high degree of molecular homogeneity and finer powders with greater surface area. They stabilized the color between 800 and 1100 °C and showed the absorption band in the range of 650-750nm, having characteristics of the red color [75].

Guo. et al. prepared the  $\text{CaFe}_2\text{O}_4$  nano-cubes by hydrothermal synthesis method for the formaldehyde sensor. The  $\text{CaFe}_2\text{O}_4$  nano-cube-based sensor exhibits strong stability to 30 ppm formaldehyde at 300°C, high gas response (16.50), quick response recovery time (153 s, 54 s), and excellent humidity resistance [76]. Zhang. et al. synthesized calcium iron oxide via a solution combustion synthesis (SCS) using glycine as a fuel. Their synthesized material photo-degraded the methylene blue (MB) because of its high photo-activity due to small particle size and high surface area [77]. Knyazev. et al. prepared

orthorhombic calcium iron oxide by solid-state synthesis method in air and helium atmosphere, which can be used as a gas analyzer [78].

$\text{CaFe}_2\text{O}_4$  is also used as a photocathode for water splitting and hydrogen evolution. Gómez. et al. prepared the thin films of  $\text{CaFe}_2\text{O}_4$  on electrodes and characterized them photoelectrochemically for hydrogen generation, and investigated further using electrochemical impedance spectroscopy (EIS). This analytical technique helps to get information about photoelectrodes' behavior and investigate the defects on the surfaces of the photoelectrodes [79]. Wang. et al. prepared  $\text{MFe}_2\text{O}_4$  (**M= Mg, Ca, and Ba**) nanoparticles by two different routes and studied their electrochemical and optical properties by changing calcination temperature, the chosen synthesis method, and the oxidation state of the chromophore ion, and divalent cation (M) [80].

For better performances, highly stable electrodes are the need for lithium-ion batteries. Han. et al. prepared the porous  $\text{CaFe}_2\text{O}_4$  by the simple sol-gel method, which showed extraordinary performance, including the high capacity (a capacity of  $816 \text{ mAh g}^{-1}$  at  $0.1 \text{ A g}^{-1}$ ) and excellent cyclic stability (capacity retention of 87% at  $0.5 \text{ A g}^{-1}$  after 1000 cycles and capacity retention of 80% at  $1 \text{ A g}^{-1}$  after 900 cycles). This study can be helpful in the generation of ultra-stable anodes for LIBs [81]. Lee. et al. demonstrated the excellent electrochemical performance of porous  $\text{CaFe}_2\text{O}_4$  anode delivering a discharge capacity of  $561 \text{ mAh g}^{-1}$  after 150 cycles even at a current density of  $200 \text{ mA g}^{-1}$  synthesized by the SCS method. The specific discharge capacity obtained after 500 cycles at  $500 \text{ mA g}^{-1}$  was  $437 \text{ mA h g}^{-1}$ , indicating better stability and performance [82]. Kenfoud. et al. studied the photoelectrochemical properties of spinal  $\text{CaFe}_2\text{O}_4$  and its application to oxidation of Blue 41, and a decrease of 80% was obtained within 3 hours under solar light of  $980 \text{ Wm}^{-2}$ . Also, they showed that the synthesis of  $\text{CaFe}_2\text{O}_4$  by nitrate route is much more beneficial [83].

Ida. et al. prepared p-type photocathodes for hydrogen and oxygen production under light without external voltage. The open circuit voltage was 0.97V, the current density was  $200 \mu\text{A/cm}^2$ , and the amount of oxygen and hydrogen produced was 70 and 4 micromoles [84]. Marschall. et al. prepared a p-type photocathode material that is highly pure and crystalline, having macropores like sponges via a straightforward solution-based

microwave reaction method. They also showed the photocurrents produced under illumination up to 600nm [85]. Marschall. et al. used a simple sol-gel method to synthesize a 250 nm thin film, a p-type photocathode having hierarchical pore-type morphology. It was also shown that photo electrocatalytic performance is limited because of the formation of calcium carbonate and charge recombination [85]. Yamaguchi. et al. revealed the excellent electrochemical properties of oxygen evolution reaction (OER) from iron and calcium-based bimetallic oxide even more than  $\text{IrO}_2$ . DFT expressed that this tremendous OER activity is because of the formation of O-O the bond between two iron sites on the catalyst's surface [86].

Bahoura. et al. demonstrated the ultra-stability of porous  $\text{CaFe}_2\text{O}_4$  anodes by increasing fuel-to-oxidizer ratios and calcination temperature. They claimed that a high temperature of around 900 °C is necessary for highly crystalline material for the increased capacities at high current densities around 1000  $\text{mA}\cdot\text{g}^{-1}$  and cyclic stability in the long term [87]. Porous  $\text{CaFe}_2\text{O}_4$  prepared by this solution combustion synthesis gave the electrodes high purity, stability, and capacities, which are useful for Li-ion batteries. Bahnemann. et al. fabricated the photoanodes of p-  $\text{CaFe}_2\text{O}_4$  / n- $\text{Fe}_2\text{O}_3$  by film processing technique without using any template. EIS showed that increased charge carrier density and decreased charge transfer resistance are the reason for a 100 % higher photo-current than hematite alone. The performance of photoelectrochemical water oxidation was further enhanced by using the CoPi catalyst because it makes the electron transfer easy at the interface of the electrode/electrolyte [88].

## **1.6. Analysis of Electrochemical Properties:**

The performance and stability of synthesized material in terms of its application in water splitting can be analyzed by well-known techniques such as cyclic voltammetry (CV), chronopotentiometry (CP), chronoamperometry (CA), Tafel slope analysis, and multi-step Chronopotentiometry (m-CP). A piece of brief background knowledge about these prestigious techniques is given below.

### 1.6.1. Cyclic Voltammetry:

Cyclic Voltammetry is the most convenient technique to get information about redox species. In this technique, voltage is usually applied from a negative to a positive potential, the response current is recorded, and the resulting plot is known as a voltammogram. A saturated calomel electrode (SCE) or silver/silver chloride electrode can be used as a reference electrode, and the reference electrode controls the working electrode's potential (synthesized material).

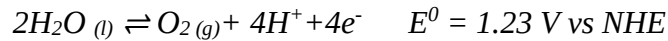
The current, caused by the oxidation of specie while moving towards more positive potential, is known as the anodic current and vice versa for the cathodic current. The voltages at which peak current is produced are known as anodic and cathodic voltages, and their average value is equivalent to the oxidation potential of redox species. [89][90]

### 1.6.2. Chronopotentiometry and Multistep- chronopotentiometry:

This technique is extremely useful for the calculation of overpotentials. Overpotential is the difference between the theoretical OER potential and the actual potential for reaction occurrence at a current density of question. Chronopotentiometry is the technique in which a constant current is applied, and the working electrode's potential is monitored with respect to a reference electrode for a particular time duration [91].

In multistep-chronopotentiometry, a constant current is applied incrementally for a different duration in each step, and the potential is monitored in response. Using the Nernst equation, values of overpotentials can be calculated theoretically for a given pH.

The chemical equation for water oxidation in an acidic medium is given as:



In this thesis work, electrochemical measurements were carried out by using 1M KOH, having a pH value of 13.6. The standard potential values of reaction conducted in electrolytes having pH 13.6 can be determined as:

$$E = E^0 - \frac{RT}{nF} \log P_{O_2} [H^+]^4$$
$$E = E^0 - \frac{0.0592}{4} \log 10 P_{O_2} [H^+]^4$$

Where  $[H^+] = 10^{-14}$  M and  $P_{O_2} = 1 atm$

$$E = 0.40V$$

This equation demonstrates that the minimum required voltage for this reaction is less in basic media as compared to acidic media. The overpotential values calculated in this thesis by chronopotentiometry are done by subtracting this value from the measured value.

### 1.6.3. Chronoampereometry:

In this technique, a constant potential in different steps, such as square waves, is applied, and the resulting current is measured with respect to time [92]. It is used to collect information about diffusion processes and kinetics of electrochemical and chemical reactions. CA is also used for Tafel slope analysis.

### 1.6.4. Tafel Slop Analysis:

Tafel slop gives an idea about the efficiency of an electrode by its current response while applying voltage, and it also provides information about the rate-determining step in the electrochemical process, its kinetics, and the likely mechanisms [93]. The unit of the Tafel slope is mV/decade, and its lower value indicates that less overpotential is required for the reaction. **Tafel equation** is written as:

$$\eta = a + b \log j$$

In the above equation,  $a$  is a constant value,  $j$  is current density having unit  $mA/cm^2$ , and  $b$  is Tafel slop (mV/decade). The literature has several Tafel slope values for a given material, such as  $NiCo_2O_4$  needle-like nanoparticles,  $NiCo_2O_4$  nanosheets, and  $CoPi$  showed 292, 312, and 393  $mV\ dec^{-1}$ , respectively [94].  $Ru$ ,  $Ru-Pt$ ,  $RuO_2/TiO_2$   $Ru-Ir$ ,  $Ir$ ,  $Pt$ ,  $Ir-Pt$  showed 41, 120, 66, 74, 85, 90, and 210  $mV\ dec^{-1}$ ,  $Ru_{0.7}Ir_{0.3}O_2$  showed to be the best electrocatalyst for OER, and pure  $RuO_2$  and  $IrO_2$  showed a Tafel slope of 40  $mV\ dec^{-1}$  and 60  $mV\ dec^{-1}$ , respectively [96].

Dag et al. have comprehensively analyzed the electrochemical properties of metal cobaltite. Specifically, they have investigated the tafel slope values for  $NiCo_2O_4$ ,  $MnCo_2O_4$ , and  $ZnCo_2O_4$  after calcination at 300 °C, reporting values of 63, 62, and 59  $mV/dec$ , respectively. The group also examined the tafel slopes for these samples at higher temperatures.[67]

Furthermore, the researchers reported the tafel slope values for  $m\text{-LiMn}_{2-x}\text{Co}_x\text{O}_4$ , where  $x$  is 0.1 for each value. The Tafel slopes ranged from 130 to 65 mV/dec, with values of 130, 115, 72, 65, 64, 66, 64, and 65 mV/dec reported. This information provides valuable insights into the electrochemical behavior of cobaltites, which can be useful for designing and optimizing electrode materials for various energy storage and conversion applications.[65]



# Chapter 2

## 2. Experimental Section

### 2.1. Chemicals:

In this study, all the chemicals were used without any purification. The chemicals used in this thesis work are listed below.

Metal salts used in this study are Calcium nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 99%, Sigma-Aldrich), iron (III) nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , >98%, Sigma-Aldrich), calcium chloride ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , >99%, Merck), iron (II) chloride ( $\text{FeCl}_2$ , 98%, Sigma-Aldrich). Cetyltrimethylammonium bromide,  $[(\text{C}_{16}\text{H}_{33})\text{N}(\text{CH}_3)_3]\text{Br}$  (CTAB), >98%, Sigma-Aldrich) as charged surfactant and decaethylene glycol mono-dodecyl ether ( $\text{C}_{32}\text{H}_{66}\text{O}_{10}$ , Sigma-Aldrich, denoted as  $\text{C}_{12}\text{EO}_{10}$ ) used as a non-ionic surfactant.

### 2.2. Synthesis of Mesoporous Materials:

#### 2.2.1. Preparation of Aqueous $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ - $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ - $\text{C}_{12}\text{EO}_{10}$ -CTAB Solution:

The surfactants, 0.287g CTAB, and 0.5g  $\text{C}_{12}\text{EO}_{10}$ , are dissolved in 5g deionized water and stirred for 45 minutes to get a homogenized solution. Afterward, metal salts (0.373g  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and 1.27g of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) are added to this solution and stirred for 15-20 min to obtain a clear solution.

### **2.2.2. Preparation of Aqueous $\text{Ca Cl}_2 \cdot 4\text{H}_2\text{O}$ - $\text{Fe Cl}_2$ - $\text{C}_{12}\text{EO}_{10}$ -CTAB Solution:**

In this case, salts (0.232 g  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  and 0.400 g  $\text{FeCl}_2$ ) are dissolved first in 5 g de-ionized water. After that, 0.5 g of conc. HCl is added to get a clear solution before the addition of surfactants CTAB (0.287 g) and  $\text{C}_{12}\text{EO}_{10}$  (0.500 g).

### **2.2.3. Preparation of Lyotropic Liquid Crystalline Mesophases (LLC) on Different Substrates and $\text{CaFe}_2\text{O}_4$ Thin Films:**

To investigate the formation of mesophases using x-ray analysis, a small amount of solution was dropped on a microscope glass slide (7.5 cm x 2.4 cm) and FTOs and spin-coated at 2000 rpm for 10 seconds. (LLC-A)

The dip-coating technique was used to fabricate the working electrodes used for electrochemical applications. (LLC-B)

The clear solution was also drop-casted on microscope slides for further characterization. (LLC-C).

All the mesophases mentioned above were calcined for 1 hour at different temperatures between 300 and 700 °C. After calcination, LLC-A coated on FTOs was used for electrochemical characterization and SEM imaging. The powders scrapped from glass slides of calcined LLC-C were used for  $\text{N}_2$  (77K) adsorption-desorption and powder x-ray (PXRD) measurements.

## **2.3. Instrumentation:**

### **2.3.1. X-Ray Diffraction (XRD) Analysis:**

To confirm the formation of LLC mesophases, the Rigaku Miniflex x-ray diffractometer was used, consisting of a source of x-ray,  $\text{Cu K } \alpha$  ( $\lambda=1.5405 \text{ \AA}$ ), operated at 30 kV and 15 mA at small angles ( $1-5^\circ$ ,  $2\theta$ ) with a step size of 0.01 and a scan rate of 1 degree per minute. Time-dependent patterns were collected during the aging of the samples. To confirm the salt crystallization, high-angle data were collected between  $10$  and  $80^\circ$ ,  $2\theta$ , with the same parameters mentioned above.

Using a Panalytical multipurpose X-Ray diffractometer configured with a  $\text{Cu K } \alpha$  source ( $1.54056 \text{ \AA}$ ), operating at 45 kV and 40 mA current, the high angle measurement ( $10-80^\circ$ ) for powders (scratched from microscopic glass slides) was carried out.

### **2.3.2. Attenuated Total Reflection Fourier-Transform Infrared (ATR-FTIR) Spectroscopy:**

A drop of solution was put on the diamond ATR crystal and followed the time-dependent LLC formation using a Bruker Alpha Platinum spectrometer. The resolution of the spectrometer is  $4\text{ cm}^{-1}$ , and the number of scans for each measurement was 32 in the range of  $400\text{--}4000\text{ cm}^{-1}$ . Also, this instrument was used to analyze powders of mesoporous products obtained at different temperatures.

### **2.3.3. X-Ray Photoelectron Spectroscopy:**

XPS spectra were obtained for the materials calcined at different temperatures to determine the oxidation state of the elements and compositions of the synthesized material. For this purpose, a powder sample was placed on a sample holder and made a connection with a metal ribbon to make a connection for electron flow. The source used for this analysis is Thermo-scientific K-alpha equipped with Al  $K\alpha$  source (1486.68 e.V.). All the measurements were carried under high vacuum conditions with a spot size of  $400\text{ }\mu\text{m}$ . At the end of each measurement, all the spectra are calibrated with respect to C 1s peak at 284.5 e.V.

### **2.3.4. $\text{N}_2$ (77K) Adsorption-Desorption Isotherms:**

$\text{N}_2$  adsorption-desorption isotherms provide information about materials' porosity, pore size, and surface area. The powders obtained from glass slides at different temperatures were dehydrated under vacuum for 3 hours at  $200\text{ }^\circ\text{C}$  to eliminate any volatile species and then installed to the analyzer to collect the isotherms.

The surface area of each sample was determined using the first 5 to 6 points of the isotherm in the range of 0.05 and 0.3 atm. The Brunauer-Emmett-Teller (BET) analysis method was used for evaluating the surface area, and Barrett-Joyner-Halenda (BJH) method was used for determining average pore size from the desorption isotherms.

### **2.3.5. Scanned Electron Microscope (SEM)–Energy Dispersive X-ray Spectroscopy (EDX):**

To get an idea about the material's morphology, SEM images of the CFO powders, calcined at different temperatures and scratched from these glass slides, were recorded

using an FEI-Quanta 200 FEG at 20 kV with a spot size of 3.0. EDX measurements were also carried out by using the same samples to get information about the atomic ratios of elements using the EDX detector attached to the microscope.

#### **2.3.6. Transmission Electron Microscopy (TEM):**

The clear solution was spin-coated on microscope glass slides and calcined at various temperatures. Afterward, the powder was scrapped from glass slides and ground in ethanol in a mortar. Finally, to disperse the sample in ethanol, sonication was done for 30 minutes, and a drop of liquor was dropped on a carbon-coated copper grid under a UV lamp for fast evaporation of ethanol. This grid was used for imaging using a high-resolution transmission electron microscope (HR-TEM) of JOEL JEM 2100F operating at 200kV.

#### **2.3.7. Polarized Optical Microscopy (POM):**

To capture the images of the LLC mesophases coated on microscope slides, we used Polarizing Optical Microscope (ZEISS Axio Scope A1) at various magnifications.

#### **2.3.8. Electrochemical Measurements:**

The electrochemical measurements were performed to elucidate the electrochemical properties of the mesoporous CFOs and to evaluate the electrode performance towards water oxidation. For almost all the electrochemical measurements, graphite-coated electrodes were used. For the fabrication of the working electrode, a 3 cm long graphite rod is used, and the dip coating technique was employed to coat 1 cm of the graphite rod. After dip coating, the coated rod is aged for one minute to evaporate its excess solvent and then calcined for 1 hour at different temperatures. The electrochemical setup used in this study involves three electrodes, and all the measurements were done using Gamry Instrument, Potentiostat (Model Number: PC14G570). The silver-silver chloride (Ag/AgCl (3 M KCl)) electrode was used as the reference electrode, and the potentials are reported as normal hydrogen electrodes (NHE) after conversion. CFO-coated graphite electrodes, calcined at different temperatures, were used as working electrodes. The electrolyte used in all electrochemical experiments throughout this thesis is 1M KOH solution. Before doing all the experiments, nitrogen gas was purged in the electrolyte

solution to remove the dissolved oxygen gas. The electrochemical setup is shown in Figure 2.1.

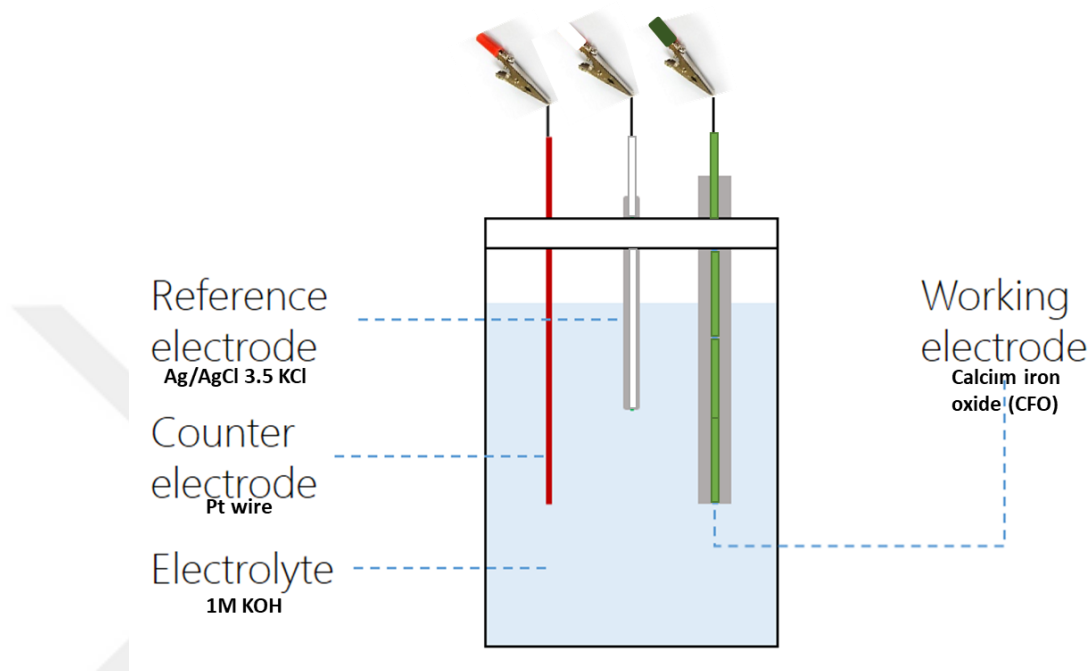


**Figure 2. 1.** Schematic diagram of an electrochemical set up.

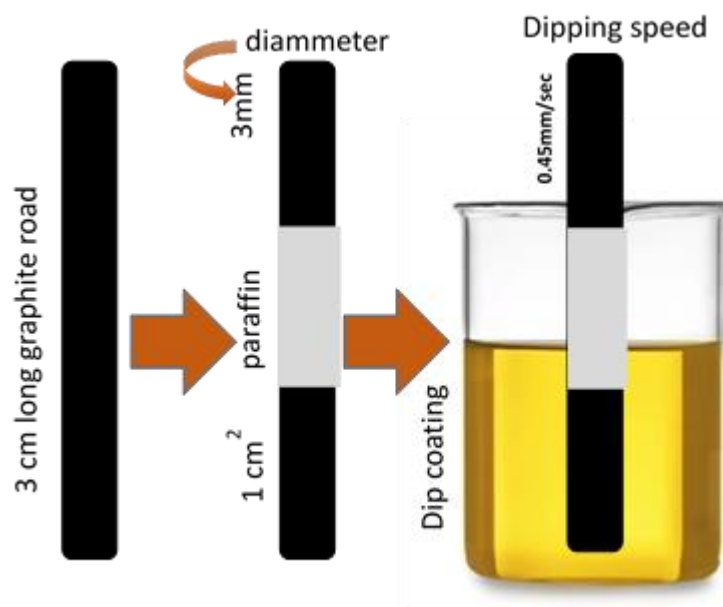


**Figure 2. 2.** Schematic representation of fabrication of working electrode by dip coating technique.

For each temperature, five electrodes were prepared and used for electrochemical measurements. For instance,

- 3 CVs for fresh electrodes,
- multistep chronoamperometry (CA) for Tafel slope analysis (0.3-0.7V),
- then another 3 CVs,
- chronopotentiometry (CP) at 1 mA for 2 hours,
- 3 more CVs,
- chronopotentiometry (CP) at 10 mA for 2 hours, and
- 3 more CVs.

2<sup>nd</sup> electrode was used for 100 cycles of cyclic voltammetry, and 3<sup>rd</sup> electrode was used for multistep chronopotentiometry (mCP). The 4<sup>th</sup> electrode was used for 200 cycles for surface analysis, and scan-rate-dependent measurements were done for the same electrode. The 5<sup>th</sup> electrode (fresh) was used for scan-rate dependent measurements as a new.

#### **2.3.8.1. Cyclic Voltammetry (CV):**

In this study, one electrode was prepared for each temperature and used for 100 cycles (scan rate of 50 mV/sec) of CVs, and for all the CVs except scan-rate dependent measurements, the potential window was chosen as -0.1-1.5V. One hundred cycles were done to check the stability of the electrode by cycling. For the 1<sup>st</sup> electrode used for a complete experiment, three cycles of CVs were recorded after each measurement, such as mCA and CP, so that we could compare the efficiency of the electrode before and after the experiment (by comparing the current density (mA/cm<sup>2</sup>) at 1.5V). In the given example below (Figure 2.3.), it is shown that we chose a -0.1-1.5V potential window for water oxidation and for 100 cycles, and for scan rate dependent measurements potential window was -0.1-0.66V.

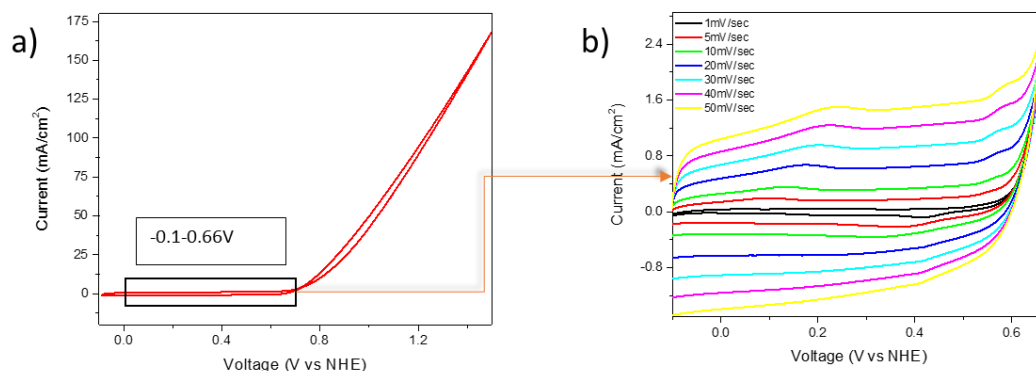


**Figure 2. 3. CVs: (a) finding a potential range for surface analysis and (b) scan rate dependent CVs, recorded moving from slow to fast (1 to 50mV / sec).**

The potential window chosen for scan rate dependent measurements was -0.1-0.66V, and it is varied as 1mV s<sup>-1</sup>, 5mV s<sup>-1</sup>, 10mV s<sup>-1</sup>, 20mV s<sup>-1</sup>, 30mV s<sup>-1</sup>, 40mV s<sup>-1</sup>, and 50mV s<sup>-1</sup>. The current density for each cycle at 0.4801V (chosen randomly) was determined and plotted against the scan rate (mV/sec). The slope of linear fit gives us an idea about the diffusion or surface reactions at the surface of an electrode being used. The value of a slope around 1.0 indicates surface controlled, while a slope around 0.5 indicates the diffusion-controlled process of charge carriers at the surface of electrodes from the plot of log current density (log I mA cm<sup>-2</sup>) versus log scan rate (log v). Here, the experimental example (Fig. 2.4.) is given for reference.

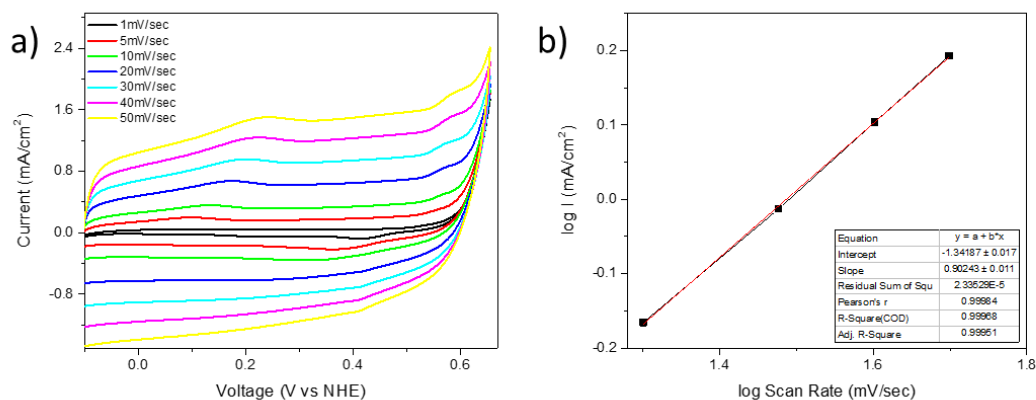


**Figure 2. 4. (a)** Scan rate dependent CVs ( $1\text{mV sec}^{-1}$  to  $50\text{mV sec}^{-1}$ ) and **(b)** plot of log current density ( $\log(I)$ ) and the log scan rate ( $\log(v)$ ).

The above linear fit has a slope of 0.90, which is an indication of a surface-controlled reaction. The details of this experiment are given in the results and discussion part.

### 2.3.8.2. Chronoamperometry (CA):

The potential window (0.3-0.7V) was predicted from the cycle of CVs, and that potential window was used for the multistep chronoamperometry (CA) experiment, which is used for the Tafel slope analysis. A minimal amount of water oxidation potentials were also included in the measurement. The potential was applied to W.E. for 5 minutes at each step (40 steps in total) with an increase of 10 mV increments. For each step, the last data point was used as the current density and plotted as “log I” on the x-axis and the measured overpotentials (V) on the y-axis, see Figure 2.5.

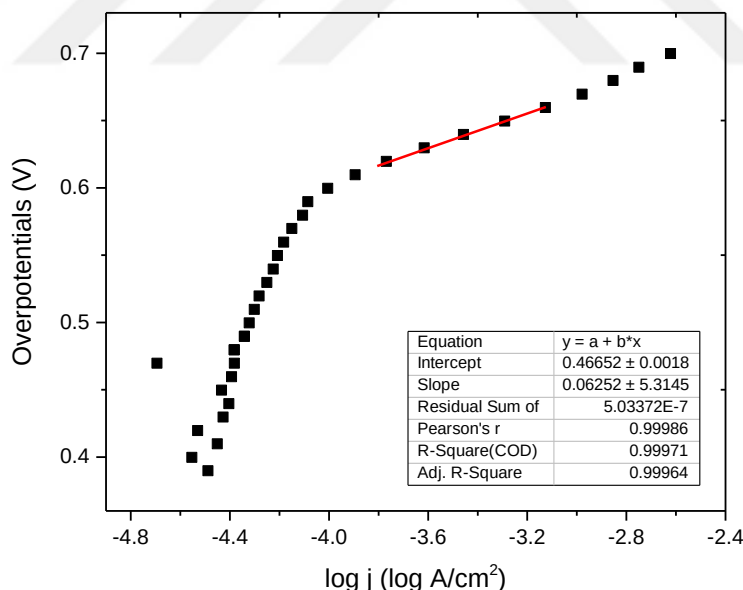


**Figure 2. 5.** Plot of log J vs. overpotentials, recorded from multistep chronoamperometry measurements.

The liner part of this plot was selected, fitted, and reported as a Tafel slope. This plot shows the Tafel slope value of  $0.062 \text{ V dec}^{-1}$ , which is reported as  $62 \text{ mV dec}^{-1}$ .

#### **2.3.8.3. Chronopotentiometry (CP):**

To calculate the overpotential, CP is the feasible technique. The current densities were fixed at 1, 10, and 100 mA cm<sup>-2</sup> for two hours, and the potentials required to maintain these current densities were recorded. The last data point was used for the calculations of overpotentials. As we used 1M KOH electrolyte in this study, so potential required for the OER in this electrolyte has to be subtracted from the potentials required for those current densities, which is 0.404V (calculated by Nernst equation).

The multistep chronopotentiometry (m-CP) experiment was also done for the 4<sup>th</sup> electrode. There are ten steps for this experiment; each step lasts 15 min. The current density for each step increased by 10 mA up to 100 mA.

# Chapter 3

## 3.1. Results and Discussion

### 3.1.1. Characterization of LLC Mesophases Prepared by using Nitrates Precursors and Two Surfactant Systems

The solutions of metal nitrate precursors ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ - $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ ) with two surfactants (10-lauryl ether ( $\text{C}_{12}\text{EO}_{10}$ ) as a non-ionic surfactant and CTAB as a charged surfactant) were prepared to investigate the formation of the lyotropic liquid crystalline mesophase (LLCM) and effect of aging of the solution on the LLCMs. The formation of LLCMs was investigated by coating the solution using spin-coating and drop-casting methods. As shown in Figure 3.1. (a), the line around  $2.05^\circ$ ,  $2\theta$ , indicates the formation of LLCMs. Other diffraction lines at  $2.28$ ,  $2.59$ ,  $2.80$ ,  $3.08$ , and  $4.09^\circ$ ,  $2\theta$ , indicate that mesophase formation is highly ordered. The line at around  $3^\circ$  indicates a surfactant (CTAB) leaching. This effect is more pronounced for the two weeks aged solution; see Figure 3.1. (b). Even with the naked eye, it can be seen the surfactant is leached out on the top of the glass side. The POM image in Figure 3.2. reveals that the mesophase has a hexagonal structure, and from several peaks, the structure may be 3D hexagonal. Initially, the mesophase structure was assumed to be a 3D hexagonal arrangement. However, some factors distort the hexagonal phase and resemble the orthorhombic

system. All the lattice parameters are unequal in the orthorhombic system; the lattice parameters we calculated from d-spacing formulas are also unequal, indicating the presence of an orthorhombic phase. The unit cell parameters calculated using an orthorhombic d-spacing system are 52.3, 57.5, and 86.4 Å for a, b, and c, respectively. The elongation along the b-axis is 9.9% more than the typical hexagonal structure. This effect can be because of certain factors, such as slight polymerization of iron species; as a result, the spherical species can be distorted to elliptical shapes and distort the structure. Due to this factor, there is the possibility of charge imbalance, and as a result, surfactant goes inside the polymerized species, and it can also play an important role in the distortion of the hexagonal phase to the orthorhombic phase. All the diffraction lines in small angle XRD measurements in this thesis are indexed according to orthorhombic d-spacing formulas. The model in figure 3.1 elucidates the b-axis's elongation and the hexagonal's transformation to the orthorhombic phase.

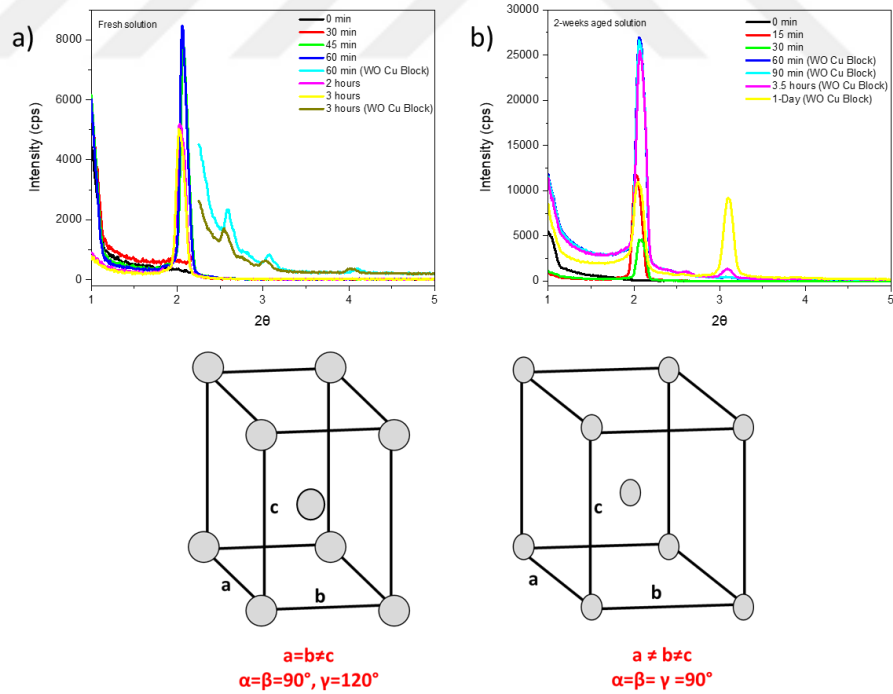


**Figure 3. 1.** Small-angle XRD patterns for LLCs (Ca:Fe, 2:4) (a) for a fresh solution and (b) for a 2-weeks aged solution.

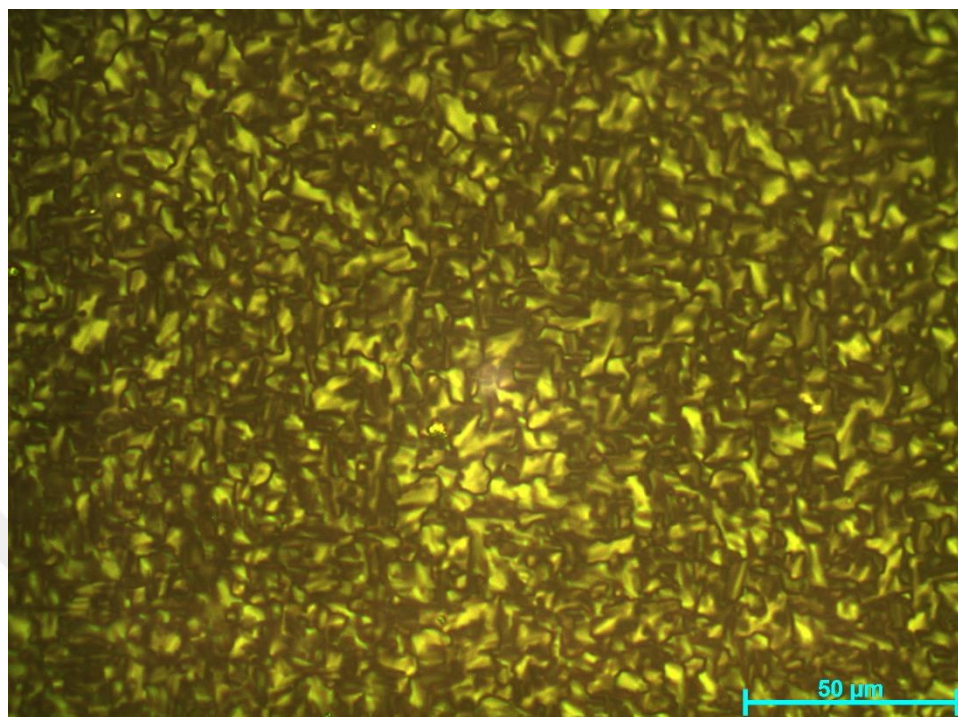


**Figure 3.** 2 POM Image of a LLCM (Ca:Fe, 2:4), drop casted on a glass slide.

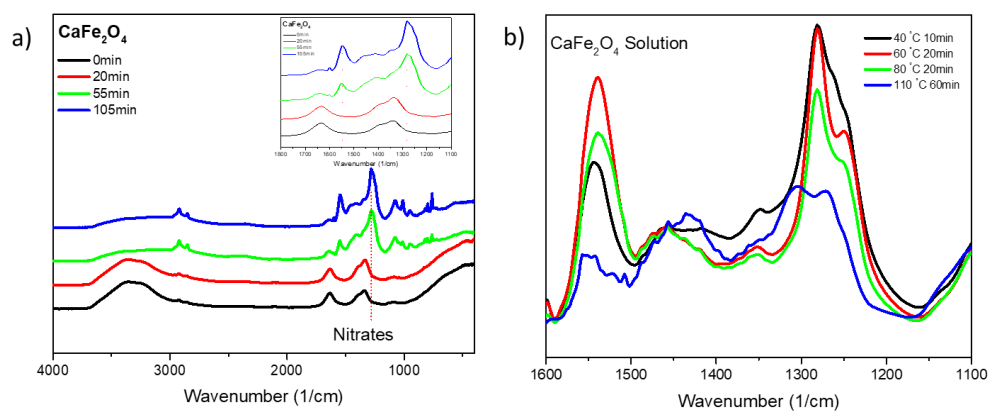


**Figure 3.3.** Time-dependent ATR-FTIR spectra of the above solution and **(b)** temperature-dependent ATR-FTIR spectra of the gel-phase.

ATR-FTIR spectra are also recorded to follow the solvent evaporation process. The nitrate species are unique in monitoring the hydrolysis and condensation process using FTIR

spectroscopy. A drop of a clear solution was put on the surface of the diamond crystal of the ATR-FTIR spectrometer, and the spectra were collected over time during water evaporation. The time-dependent and temperature-dependent measurements were carried out to elucidate the interaction of nitrate species with the metal ions during the evaporation of water. Free nitrate species have a  $D_{3h}$  symmetry, showing a peak at around  $1360\text{ cm}^{-1}$ ; when it binds to the metal ion, its symmetry changes, and the peak splits into two peaks (between  $1280$  and  $1550\text{ cm}^{-1}$ ) and can be used to monitor the hydrolysis and condensation processes. The increasing temperature on the diamond crystal decomposes the nitrate species, and the decrease in intensity of these two peaks with increasing temperature is due to nitrate decomposition. It is obvious that even at  $100\text{ }^{\circ}\text{C}$ , a considerable amount of nitrates have been decomposed, see Figure 3.3. (b).

### **3.1.2. Characterization of Mesoporous $\text{CaFe}_2\text{O}_4$ Thin Films**

Above gel-films over glass slides were calcined by directly inserting them into a pre-heated oven at various temperatures, and the samples were decoded as m-CFO-XXX, where XXX is the calcination temperature in Celsius. Figure 3.4 shows the IR spectra of the powders scrapped from the glass slides after calcination at different temperatures. The IR spectrum of m-CFO-300 reveals a formation of bicarbonates or surface carbonates. But at  $400\text{ }^{\circ}\text{C}$ , calcium carbonates are formed; the peaks at  $1421$  and  $876\text{ cm}^{-1}$  indicate its formation and correspond to asymmetric stretching and bending modes of carbonate ions.[97] The carbonates are stable up to  $600\text{ }^{\circ}\text{C}$  and start to decompose above this temperature. A considerable decrease in intensity of the peak at  $876\text{ cm}^{-1}$  in the spectrum of m-CFO-700 confirms the decomposition of carbonates, and the absence of these peaks reveals that there is no calcium carbonate anymore in the sample at  $800\text{ }^{\circ}\text{C}$ , namely m-CFO-800.

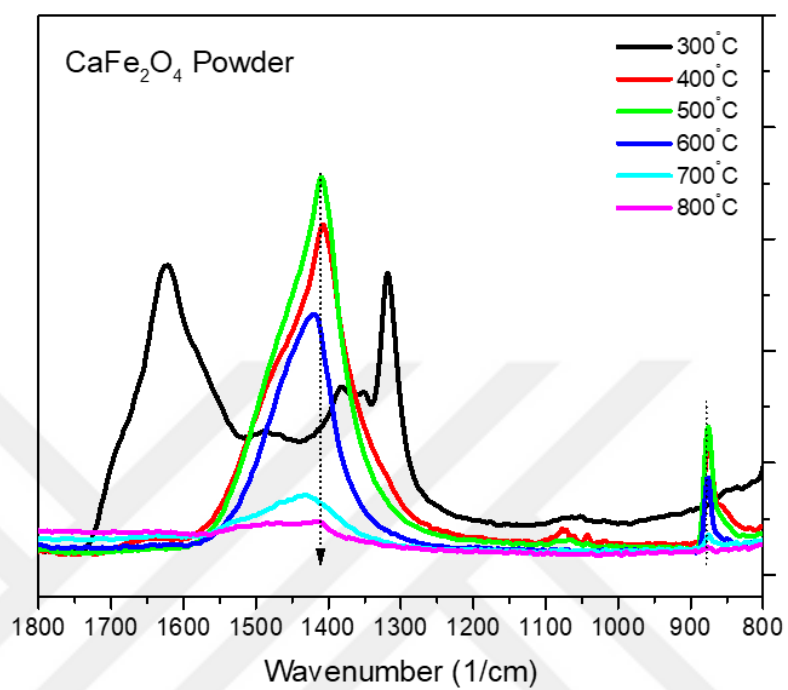


**Figure 3. 4.** ATR-FTIR spectra of CFO powders, calcined at different temperatures.

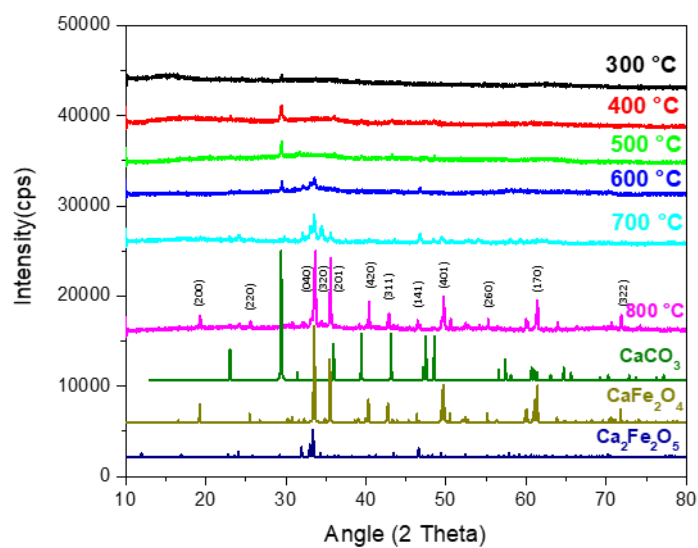


**Figure 3. 5.** Temperature-dependent wide-angle XRD patterns of the m-CFO-XXX powders.

The powders, calcined at different temperatures and scratched from the glass slides, were used to record their XRD patterns at wide angles, see Figure 3.5. The pattern shows a diffraction line at around  $29^\circ$ ,  $2\theta$ , due to carbonates. This line is persistent up to  $600^\circ\text{C}$ , which reveals the stability of carbonates compared to the patterns in Figure 3.5. The XRD data perfectly aligned with the IR data regarding the formation and decomposition of the carbonates. The diffraction lines at around  $33^\circ$  and  $35^\circ$ ,  $2\theta$ , indicate the formation of  $\text{CaFe}_2\text{O}_4$ . The structural parameters of a unit cell of CFO are  $a = 9.230$ ,  $b = 10.070$ , and  $c = 3.024 \text{ \AA}$ , having an orthorhombic structure. The line, at around  $29^\circ$ , which indicates carbonate formation, starts shifting towards a slightly higher angle, showing the formation of a calcium-deficient phase (pdf card no. 04-010-9355). Upon decomposition of calcium carbonates, calcium ions tend to incorporate into the iron lattice. The XRD pattern of iron oxide (FO) and calcium iron oxide (CFO) is almost similar, and it is hard to differentiate between FO and CFO. But the slight shift of the above-mentioned diffraction lines indicates the transformation of  $\text{Fe}_2\text{O}_3$  and  $\text{Ca}_2\text{Fe}_2\text{O}_5$  into  $\text{CaFe}_2\text{O}_4$  at  $800^\circ\text{C}$ . Because at  $700^\circ\text{C}$ , calcium iron oxide is formed but not phase pure as it contains some  $\text{Ca}_2\text{Fe}_2\text{O}_5$  particles. The line around  $29^\circ$ ,  $2\theta$ , which is the indication of calcium carbonate formation, is persistent till  $500^\circ\text{C}$ ; above that, it starts to shift towards a bit higher angles, confirming the formation of calcium deficient phase  $\text{Ca}_2\text{Fe}_2\text{O}_5$ , at  $700^\circ\text{C}$ , and finally, it is converted into CFO, and the peak at  $29^\circ$ ,  $2\theta$ , disappears. Also, it is essential to note that the diffraction lines of  $\text{Ca}_2\text{Fe}_2\text{O}_5$  do not match the lines of the  $700^\circ\text{C}$  calcined sample; instead, they all are shifted towards a lower angle. It can vary from instrument to instrument, but it is important that all the lines shift is unidirectional. In literature, CFO has been crystallized at  $1100^\circ\text{C}$  [75], but we have synthesized CFO at  $700^\circ\text{C}$ , which is not phase pure; but at  $800^\circ\text{C}$ , there is a clear formation of  $\text{CaFe}_2\text{O}_4$  (CFO). Since, up to  $500^\circ\text{C}$ , the crystalline carbonates and amorphous calcium iron oxide are formed, crystal size is calculated above  $500^\circ\text{C}$  calcination temperature. There is an increase in the sharpness of diffraction lines at higher temperatures indicating the growth of the particles. Scherer's equation was employed to evaluate the particle size at each calcination temperature, see Table 3.1. The crystal size is calculated using the line at  $33.55^\circ$  ( $2\theta$ ), and the equation is given below.

$$D(nm) = \frac{K\lambda}{\beta \cos\theta} = \frac{0.94 * 0.154056}{FWHM \cos\theta}$$

In the above equation, D is the average size of crystal domains,  $\lambda$  is the wavelength of the x-ray used during measurements, theta is the Bragg angle, K is the dimensionless shape factor having a constant value of 0.94, and  $\beta$  is the line broadening at full-width-half-maximum after instrumental broadening (instrumental broadening was evaluated using highly crystalline silicon and its diffraction line at around 33.55° (2 $\theta$ )).

| Calcination Temperature | Crystal Size (nm) |
|-------------------------|-------------------|
| 600 °C                  | 11                |
| 700 °C                  | 28                |
| 800 °C                  | 39                |

**Table 3. 1** Crystal size (nm) at different calcination temperatures (Ca:Fe, 2:4).

SEM images were also recorded to give an idea about the morphology of the m-CFOs at all temperatures. Figure 3.6 shows that the material has a film-like morphology up to 600 °C. SEM image of m-CFO-800 shows CFOs with a sphere-like and needle-like morphology. The images also show the retention of pores even at very high temperatures. Also, the sample, which was coated on the surface of FTO, was directly used to collect SEM images. The images show that the pore-walls grow (thicker pore-walls) and pores expand, keeping the film morphology, see images in Figure 3.7.

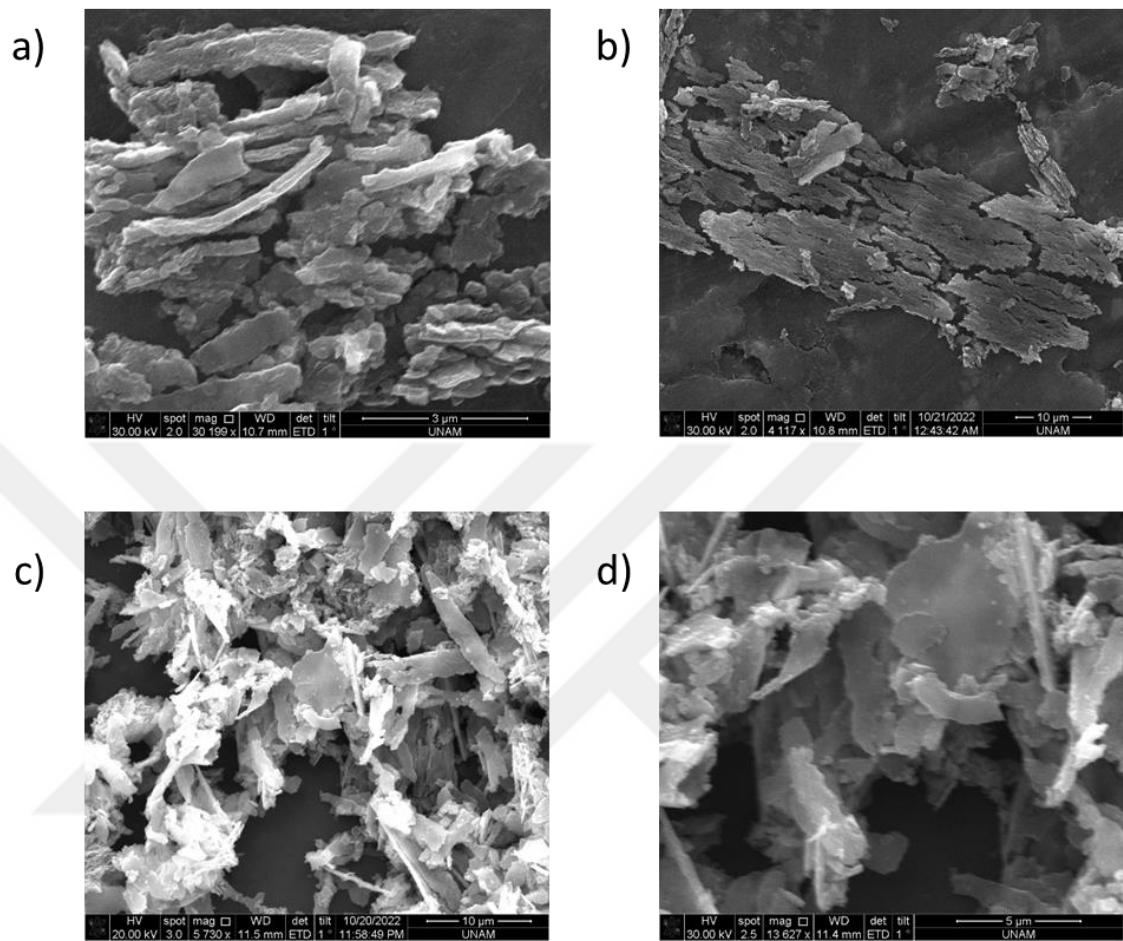


**Figure 3. 6.** SEM images of m-CFO-XXX; XXX is 300 °C with scale bars of (a) 3 μm and (b) 10 μm and 400 °C and bars of (c) 10 μm and (d) 5 μm.

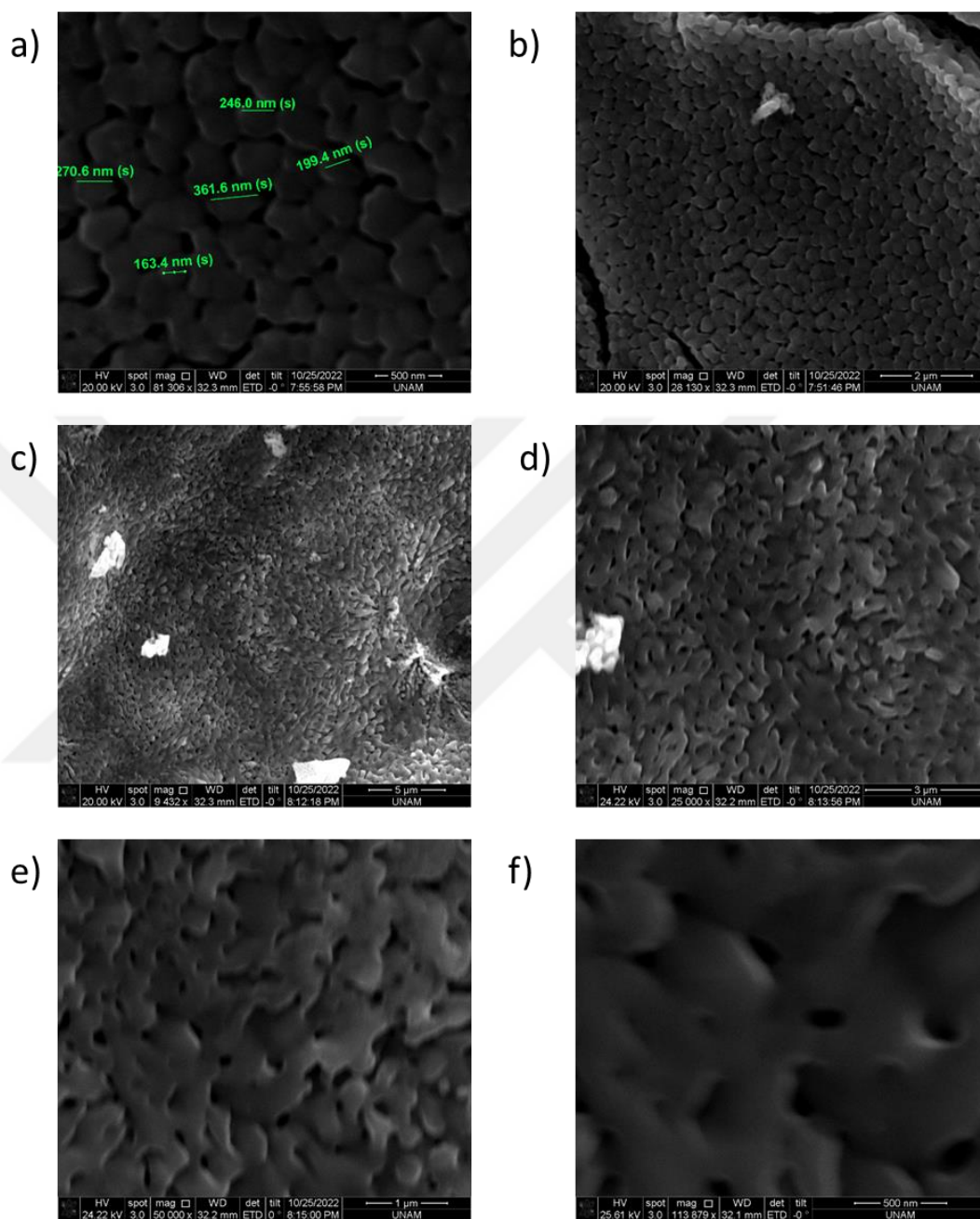


**Figure 3. 7.** SEM Images of crystalline m-CFO-800 powder at various magnification (scale bars are (a) 500 nm, (b) 2  $\mu$ m, (c) 5  $\mu$ m, (d) 3  $\mu$ m, (e) 1  $\mu$ m, and (f) 500 nm).

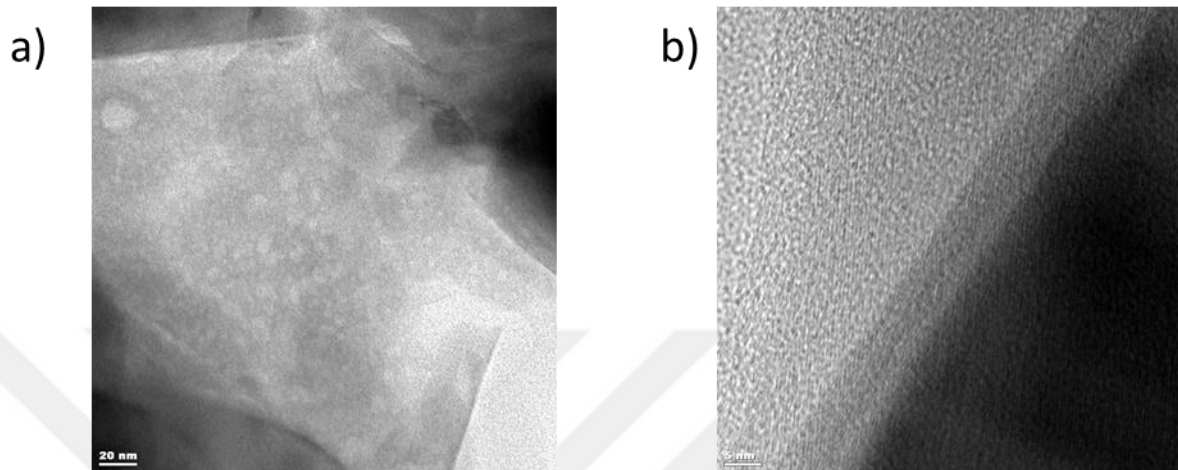


**Figure 3. 8** HR-TEM images of m-CFO-800.

The High-resolution TEM (HR-TEM) images reveal that even at such a high temperature, crystalline CFO retained a porous structure (confirmed by HR-TEM). Figure 3.8. (a) shows some regions inside the material still having a porous structure in Figure 3.8. (b), the lattice fringes are visible and reveal that the material is highly crystalline.

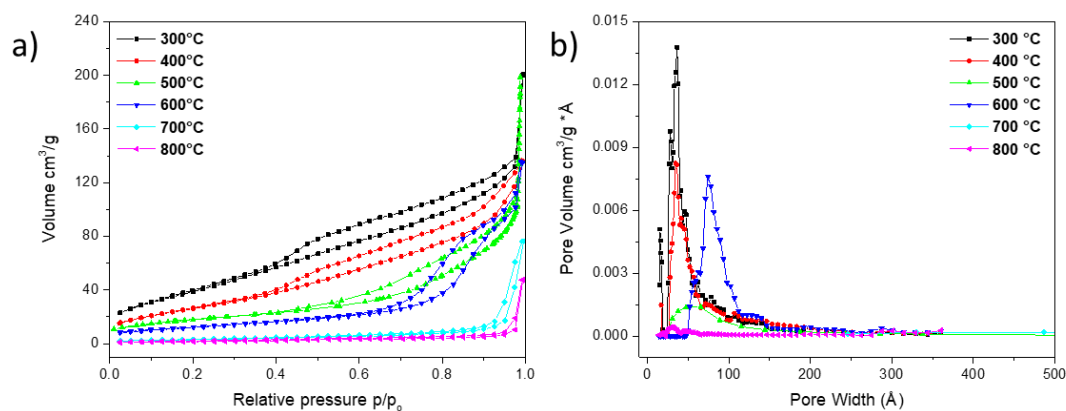


**Figure 3. 9.** (a) N<sub>2</sub> (77K) adsorption-desorption isotherms and (b) pore size distribution plots

To calculate the surface area and get an idea about pore size distribution, N<sub>2</sub> adsorption-desorption isotherms were collected. Figure 3.9 shows the isotherms and pore size distribution plots for the same powders scratched from glass slides. There is an inverse relation between calcination temperature and BET surface area. Also, with the increase of calcination temperature, the pores expand and get damaged at higher temperatures, i.e., 800 °C. The isotherms in Figure 3.9 are characteristic of mesoporous materials (type-IV). Table 3.2 lists the surface area of the material calcined at various temperatures.

| Calcination Temperature | Surface Area (m <sup>2</sup> /g) |
|-------------------------|----------------------------------|
| 300 °C                  | 145                              |
| 400 °C                  | 102                              |
| 500 °C                  | 65                               |
| 600 °C                  | 10                               |
| 700 °C                  | 9                                |
| 800 °C                  | 5                                |

**Table 3. 2.** Surface area of the m-CFO-XXXs, obtained from the N<sub>2</sub> (77K) adsorption-desorption data.

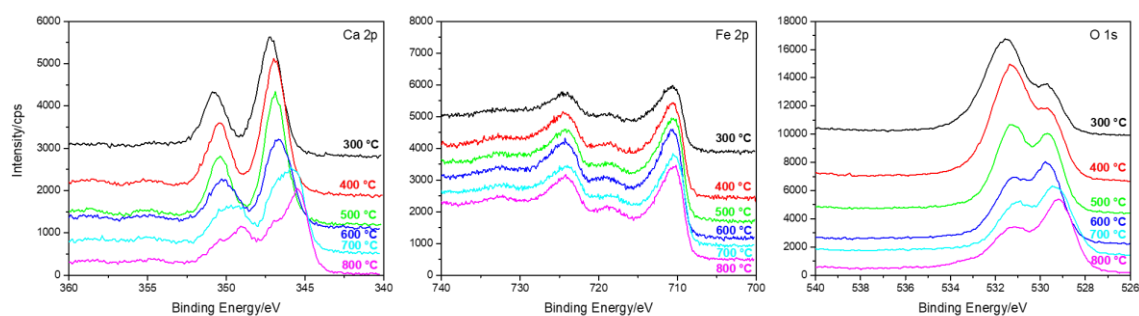


**Figure 3. 10.** XPS spectra of m-CFO-XXX, obtained at different temperatures (a) Ca-2p (b) Fe-2p, and (c) O-1s spectra.

The XPS data in Figure 3.10 also show the formation of carbonates, their decomposition, and then the formation of CaFe<sub>2</sub>O<sub>4</sub> at higher temperatures. In the XPS spectra of the Ca-

2p region, the peak at around 347 eV is assigned to calcium carbonates at 300 °C and retains up to 500 °C (stability of carbonates up to this temperature). Above 500 °C, a shift of this peak towards lower binding energy is observed and assigned to the decomposition of carbonates and the formation of Ca-O bonds in  $\text{CaFe}_2\text{O}_4$ . The above trend perfectly aligns with the IR and XRD data as it has been shown that the deterioration of carbonates starts at 500 °C and the formation of calcium iron oxide. Similarly, this peak shifts considerably to lower binding energy, confirming calcium carbonates' complete removal. At the same time, the shift of peak in the O-1s region also contains plenty of information indicating the formation of  $\text{Fe}_2\text{O}_3$  and carbonates (both in almost the same region) at a lower temperature. The peak around 710.88 e.V. indicates the presence of iron in the 3+ oxidation state, which can be attributed to  $\text{FeOOH}$  or  $\text{Fe}_2\text{O}_3$ . For sure, at high temperatures, the  $\text{FeOOH}$  cannot survive, so it may indicate iron has a 3+ oxidation state in CFO.

### **3.1.3. Mesoporous $\text{CaFe}_2\text{O}_4$ Thin Films as Electrocatalyst for Oxygen Evolution Reaction (OER)**

At first, we spin-coated a clear solution of CFO ingredients on the surface of fluorine-doped tin oxide (FTO) to fabricate the working electrodes. Then, these electrodes were calcined at various temperatures ranging from 300-700 °C, and each electrode was used for 100 cycles using cyclic voltammetry. In all cases, current density drops down with cycling, indicating electrode degradation by usage, except for the m-CFO-700, likely due to its crystallinity. Figure 3.11 a-e shows the CVs of all electrodes, calcined at all temperatures. Only 5 CVs are shown in the Figures between the 1<sup>st</sup> and 100<sup>th</sup> cycles to show the changes. They all display relatively higher overpotentials with the use of the FTO-coated electrodes. Figure 3.11(f) shows CPs plots of the electrodes, calcined at all temperatures. Similarly, only the m-CFO-700 sample remains stable during 2 hrs CP experiment even at 1  $\text{mA cm}^{-2}$  current density.

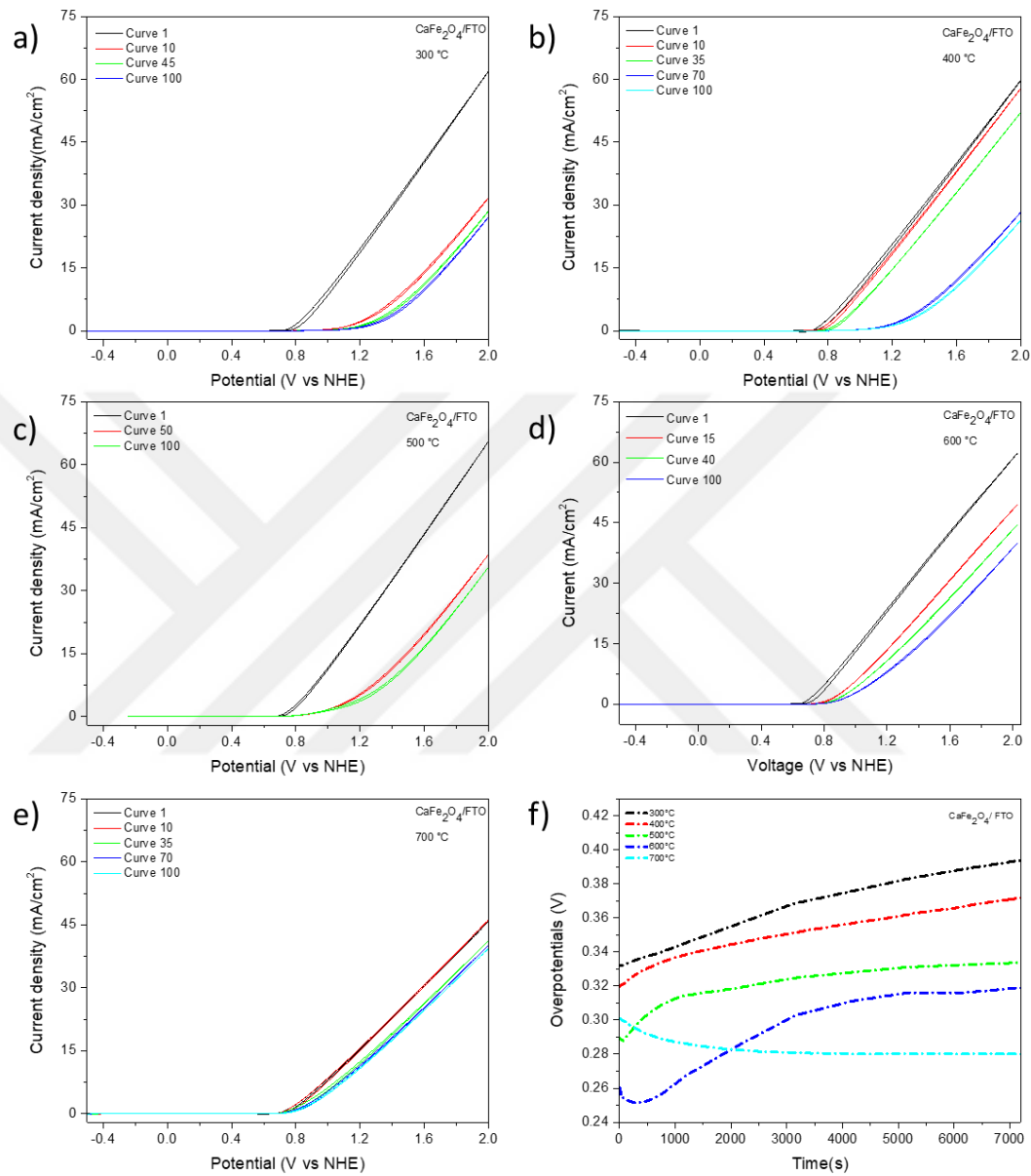


**Figure 3. 11.** (a) - (e) Multiple CVs of calcium iron oxide coated electrodes, calcined at different temperatures ranging from 300 °C – 700 °C and (f) over potentials versus time plots (CPs) of all electrodes at 1mA cm<sup>-2</sup> for 2 hours.

With the inspection of the above data, we found that the electrodes are not stable on the surface of FTO; it is the likely reason for decreasing current density with cycling. To investigate further, we compared the XPS spectra of two electrodes (fresh and the other after five cycles of CV). The spectra revealed that calcium ions are removed from the electrode surface into the electrolyte solution, which may be why the m-CFO films are not stable on the surface of the electrode. The XPS spectra of Ca-2p are given in Figure 3.12 (a). It is plausible that the increased exposure of iron to x-ray radiation, resulting from the removal of calcium from the electrode surface, may account for the observed higher intensity of iron following electrode use.

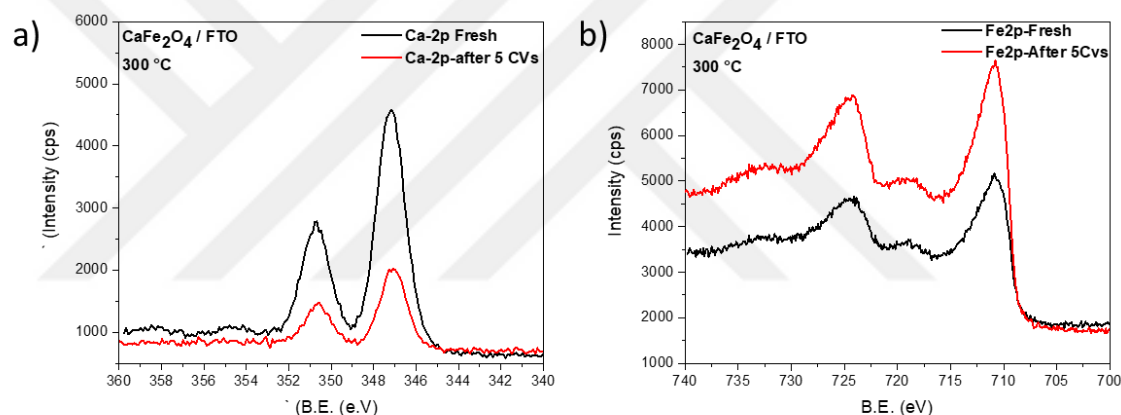


**Figure 3. 12.** XPS spectra of (a) Ca-2p and (b) Fe-2p region before and after 5<sup>th</sup> CVs.

To overcome this problem, we used a 3 cm long graphite rod with a diameter of 3 mm as a substrate for the fabrication of the anodes to investigate the electrochemical properties and efficiency of mesoporous  $\text{CaFe}_2\text{O}_4$  as an electrocatalyst in the oxygen evolution reaction (OER). The solution of ingredients was coated to one-third (1 cm) of the graphite rod and calcined as usual, and used as the working electrode in all electrochemical experiments, decoded as G-CFO-XXX (G stands for graphite rod, and XXX is the calcination temperature in Celsius).

Cyclic voltammetry (100 cycles) was used to elucidate the stability of the electrode at each temperature using the graphite-coated CFO (G-CFO-XXX). The potential window

chosen for the CVs is -0.1 V-1.5 V versus normal hydrogen electrode (NHE); see Figure 3.13.

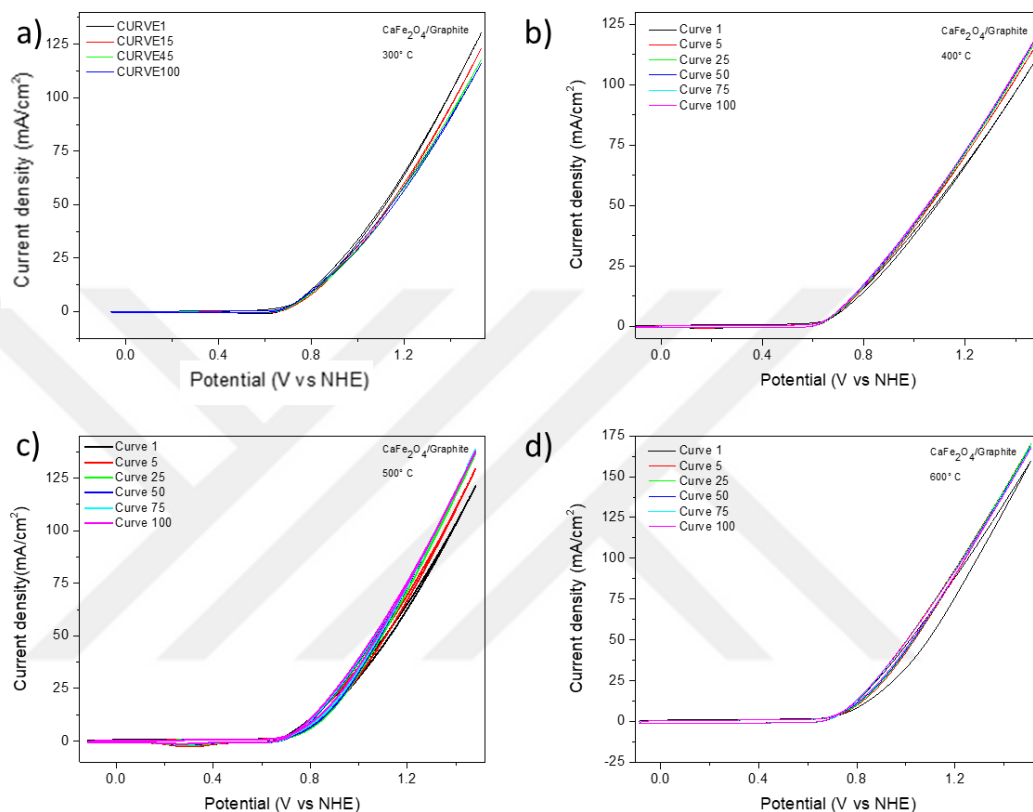


**Figure 3. 13.** Multiple CVs of  $\text{CaFe}_2\text{O}_4$  coated graphite electrodes, calcined at (a) 300 °C (b) 400 °C (c) 500 °C , and (d) 600 °C

As shown in Figure 3.13. (a), the current density decreases with cycling for the G-CFO-300 electrode, which may be because of the instability of the material on the surface of the graphite rod. The current density continuously improves in the G-CFO-400, the G-CFO-500, and the G-CFO-600 electrodes. These experiments show the stability of electrodes and improve electrode performance with use as an electrocatalyst in OER. Figures 3.14 and 3.15 show the scan rate-dependent experiments also conducted for each calcination temperature to evaluate whether the OER process is a diffusion or surface-controlled reaction. A random potential of 0.48 V was chosen for all the plots, and at this

potential, current values against each scan rate were plotted; the plot is log current density ( $\log I/\text{mA cm}^{-2}$ ) versus log scan rate ( $\log v$ ), and linear fit gives a slope for each electrode, see Figure 3.16. The slopes are 0.78 for G-CFO-300, 0.69 for G-CFO-400, and 0.71 for G-CFO-500 electrodes, and these values indicate that the reaction occurs by both processes, i.e., diffusion and surface controlled.

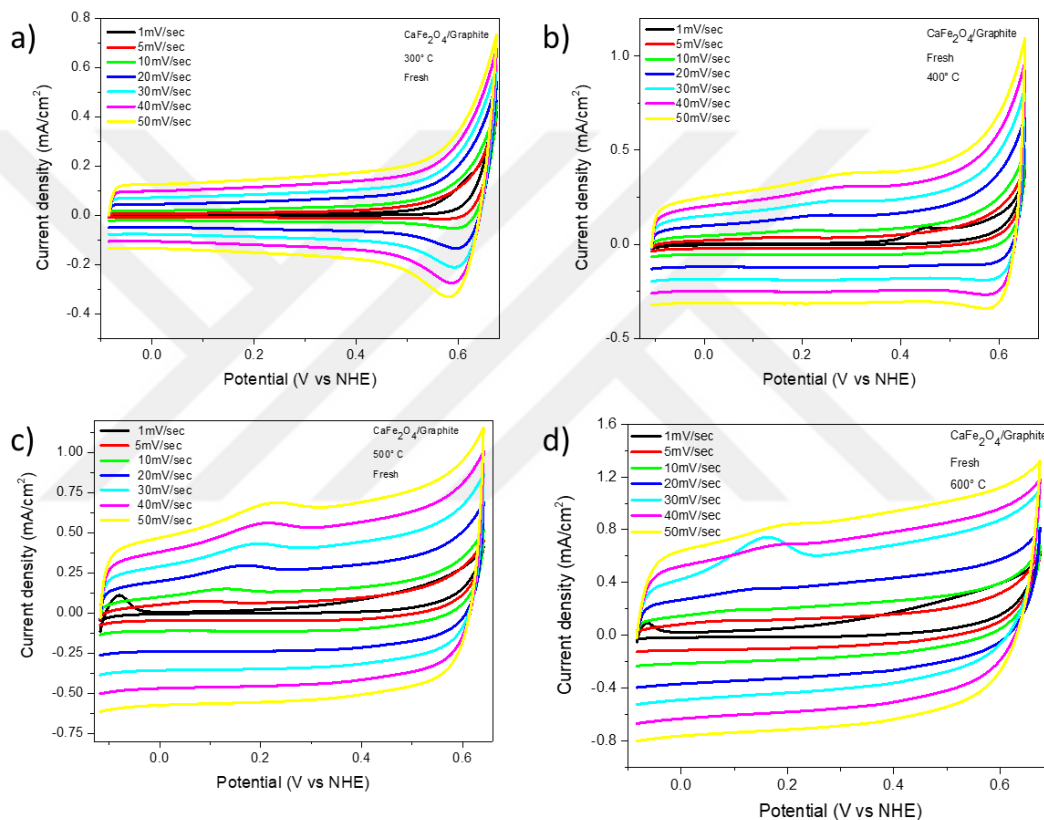


**Figure 3. 14.** Scan rate-dependent CVs of (a) G-CFO-300, (b) G-CFO-400, (c) G-CFO-500, and (d) G-CFO-600 fresh electrodes.

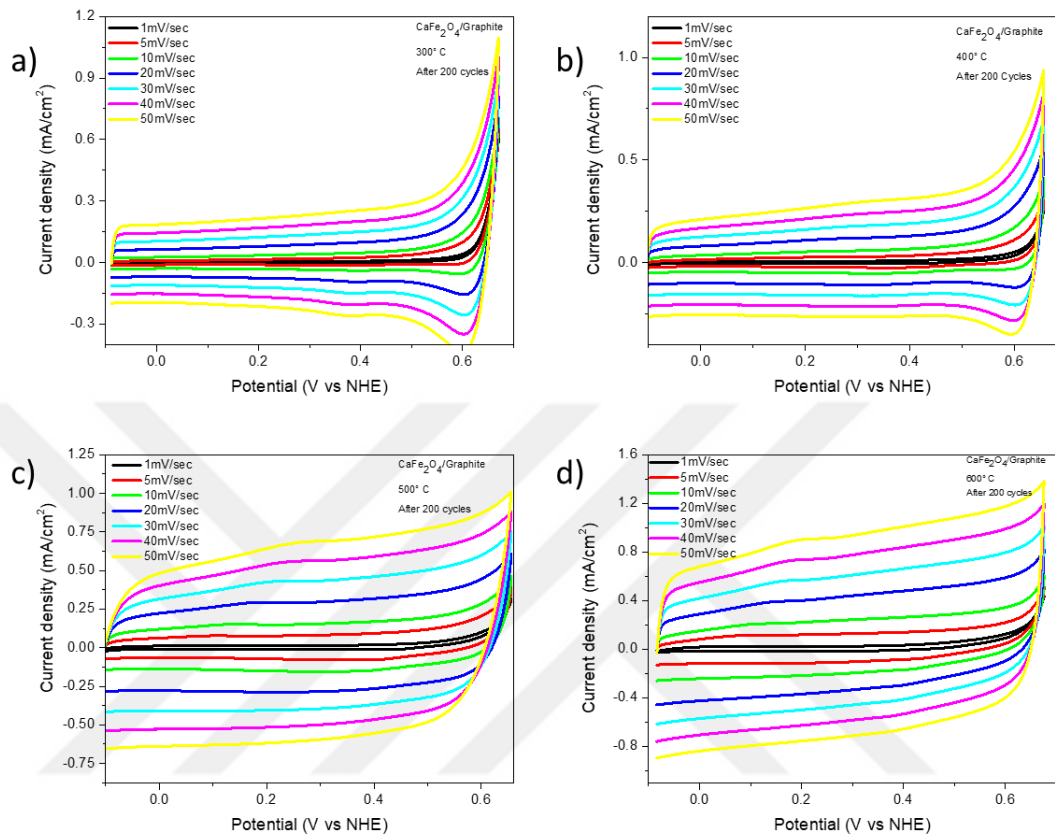


**Figure 3. 15.** Scan rate-dependent CVs of (a) G-CFO-300, (b) G-CFO-400, (c) G-CFO-500, and (d) G-CFO-600 electrodes after 200 cycles.

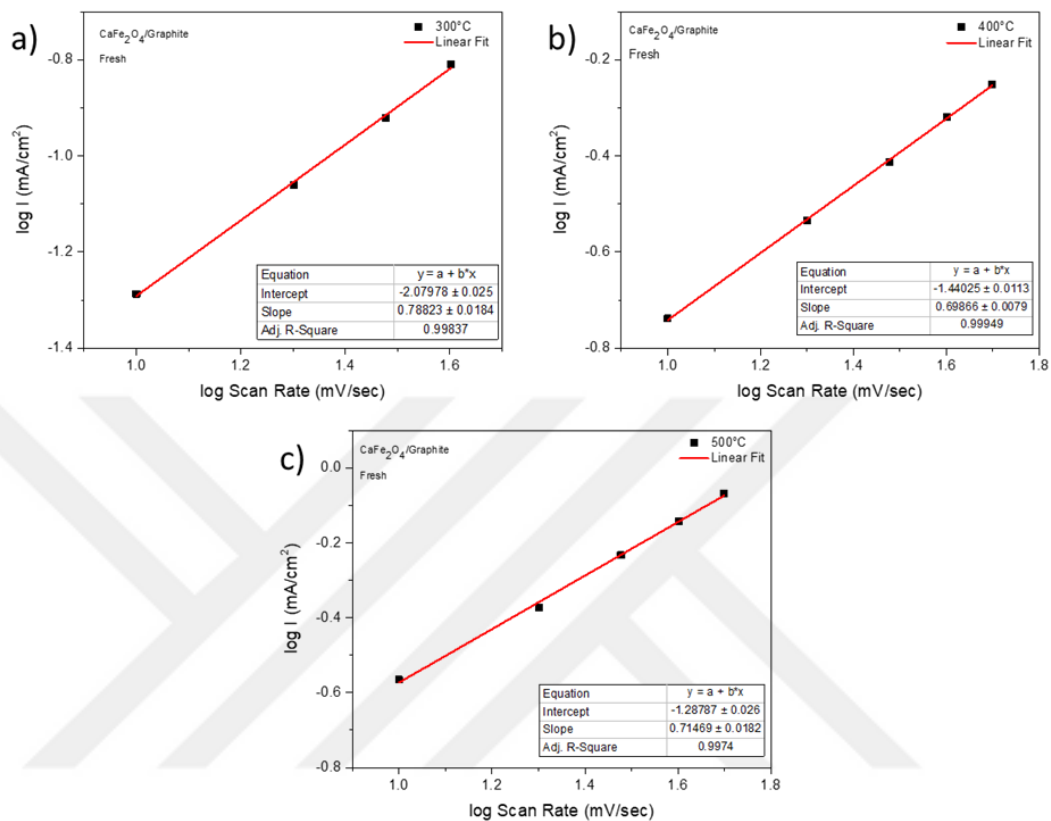


**Figure 3. 16.** Plot of log current density ( $\log I$  mA cm<sup>-2</sup>) versus log scan rate ( $\log v$ ) of **(a)** G-CFO-300, **(b)** G-CFO-400, and **(c)** G-CFO-500 fresh electrodes.

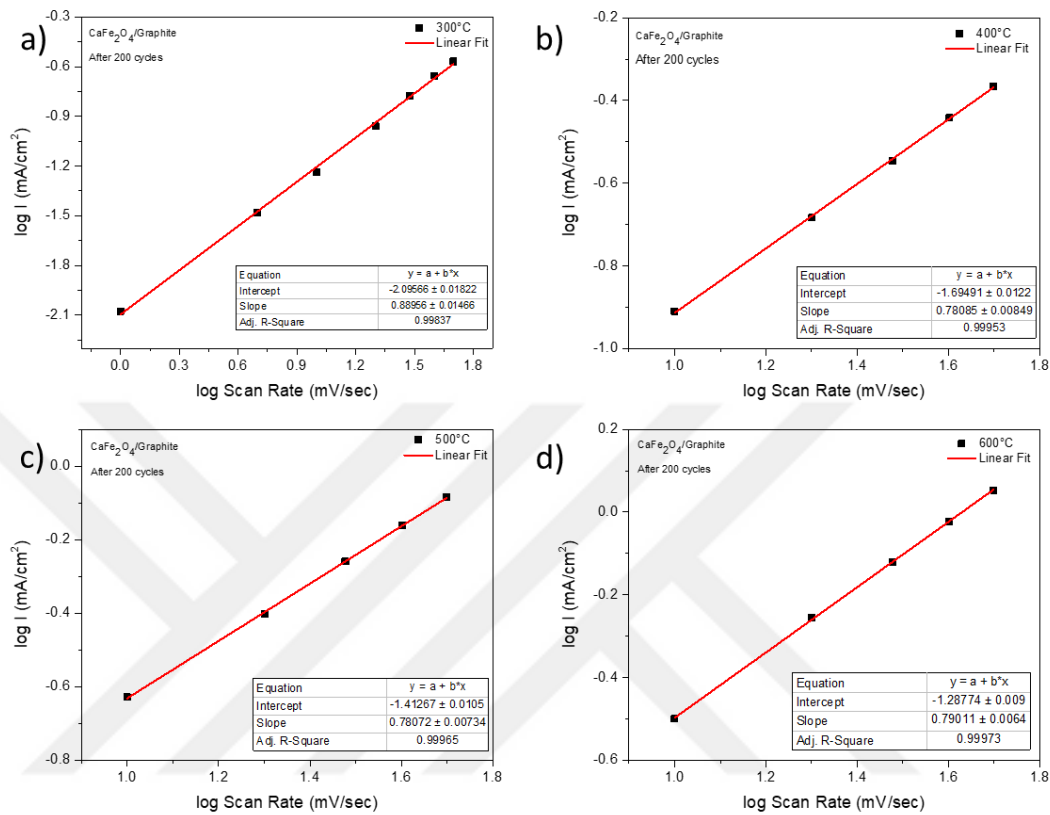


**Figure 3. 17.** Plot of log current density ( $\log I$   $\text{mA cm}^{-2}$ ) versus log scan rate ( $\log v$ ) of **(a)** G-CFO-300, **(b)** G-CFO-400, **(c)** G-CFO-500, and **(d)** G-CFO-600 electrodes after 200 cycles.

The same scan rate-dependent experiments were also repeated after 200 cycles of cyclic voltammetry (-0.1-0.66V) to evaluate the effect on the diffusion after surface usage. It is evident from Figure 3.17 that the increase in slope values after 200 CVs, the OER reactions are surface controlled.

The comparison for all the electrodes, calcined at different temperatures, is given in Figure 3.18. The performance of the electrodes is improved even with usage in harsh conditions (almost 10-12 hours' use at higher current densities). It is shown that the current densities for the water oxidation side are increasing with the usage, even under harsh conditions. It is apparent from the G-CFO-600 electrode that the current density increased drastically with the use, see Figure 3.18.

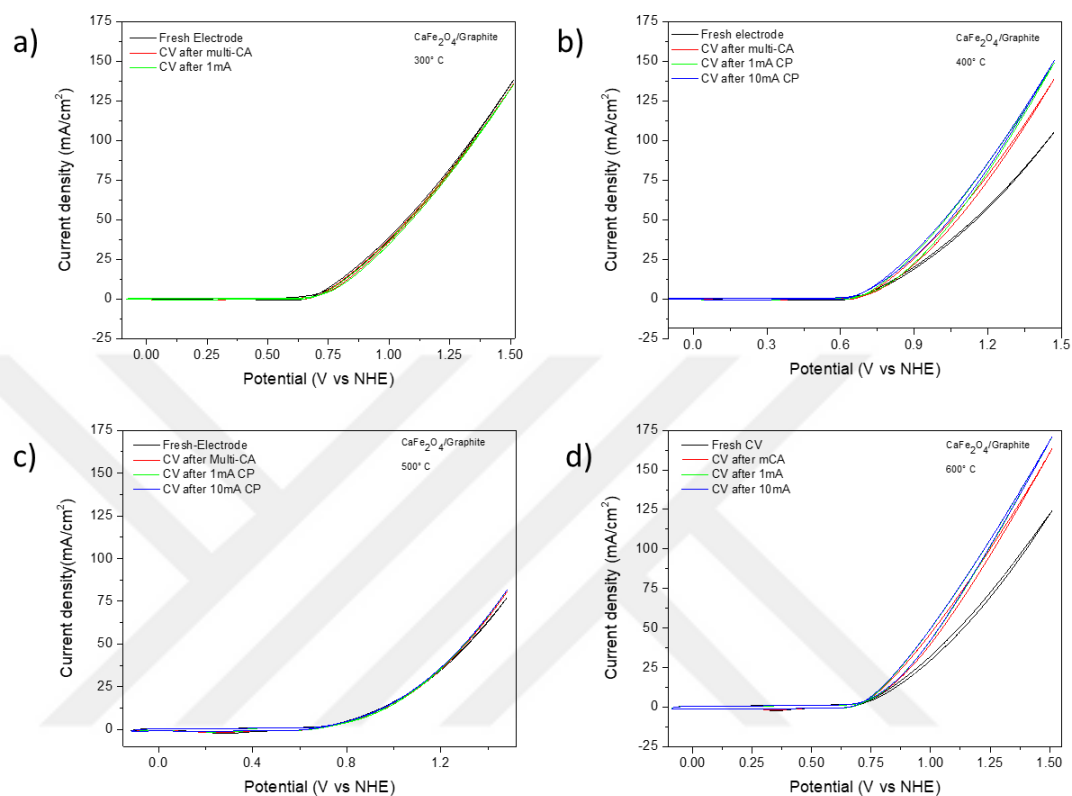


**Figure 3. 18.** Comparison of CVs after each experiment for the analysis of performance of electrodes, calcined at (a) 300 °C (b) 400 °C (c) 500 °C, and (d) 600 °C

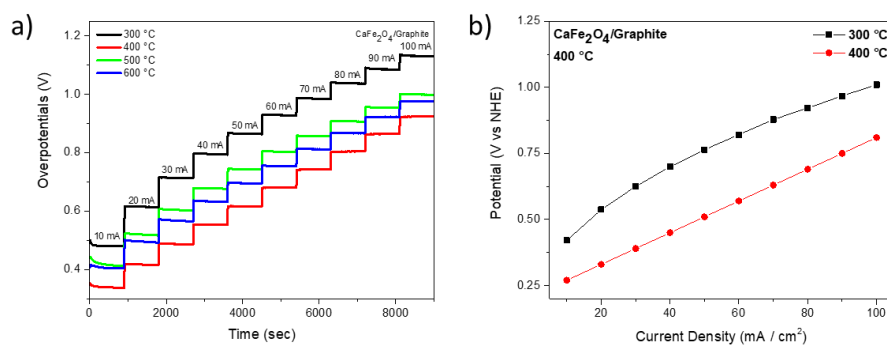


**Figure 3. 19.** Plot of multistep chronopotentiometry of all the electrodes at various current densities ranging from 10 to 100  $\text{mA}/\text{cm}^2$ . Each step took 15 minutes.

The multi-step chronopotentiometry (m-CP) experiments are conducted to calculate the overpotentials at different current densities (10-100 mA cm<sup>-2</sup>); see Figure 3.19. It is an ideal experiment to determine the overpotentials at various current densities in a single experiment. Each step consists of 15 minutes, and it is noticeable that they are not following temperature dependencies. But, over-potentials, even at high current densities, are quite low.

In Figure 3.19 (b), a potential vs. current plot is presented, which allows for the calculation of resistance throughout the duration of the electrode measurement and the assessment of its stability. It should be noted that the reported overpotentials are after tafel removal. For the 300°C calcined electrode, it can be seen that the resistance between 10 to 20mA (slope of the first two points) is higher than that of between 90 to 100mA (the last two points), indicating a decrease in resistance with usage. However, in this electrochemical experiment, 11 Ohm resistance was initially observed while using graphite as a substrate, which ultimately decreased to 4 Ohm at the end of the experiment, which seems an error. This could be attributed to a poor connection between the crocodile clips and the graphite rod, leading to a very high initial resistance. Thus, this initial resistance value may be an experimental error. In contrast, for the sample calcined at 400 °C, the slope value is consistent throughout the measurement, with a value of approximately 6 Ohm, indicating excellent electrode stability even under harsh conditions.

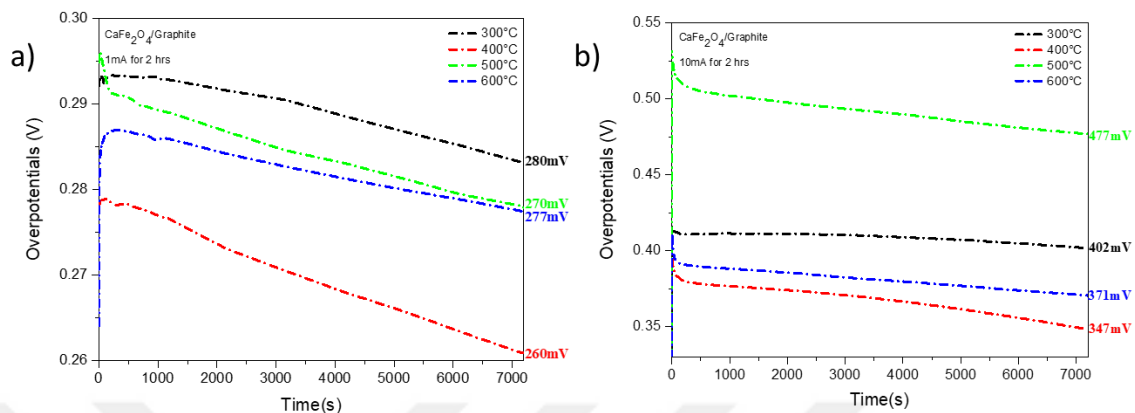


**Figure 3. 20.** Overpotentials versus time plots using chronopotentiometry (CP) at (a) 1mA cm<sup>-2</sup> and (b) 10 mA cm<sup>-2</sup> for 2 hours.

To calculate the over-potentials at 1 and 10 mA cm<sup>-2</sup>, chronopotentiometry (CP) experiments are done. At each current density, experiments were conducted for two hours, and the last point was taken as a value of overpotential (extra voltage required for OER at a desired rate). Figure 3.20 shows that overpotentials at each current density almost have the same values except for the G-CFO-500 electrode, which has a higher overpotential (at 10 mA cm<sup>-2</sup> current density). Overpotentials decay in all electrodes with usage, indicating improved performance.

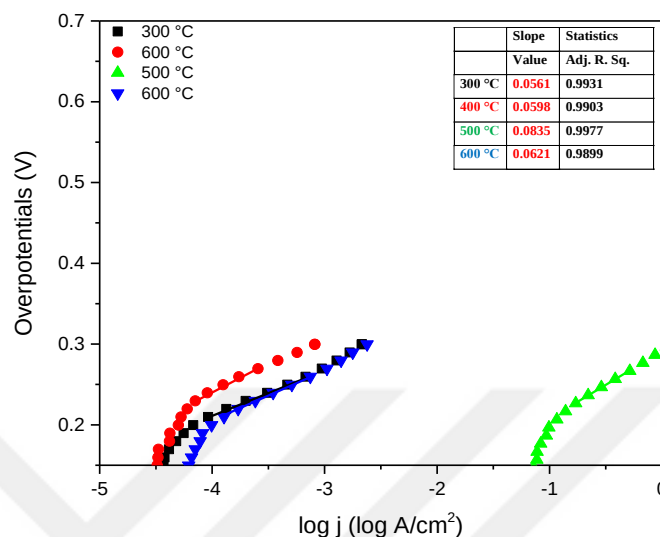


**Figure 3. 21.** Temperature-dependent Tafel slope of G-CFO-XXX electrodes.

Multistep chronoamperometry experiments are conducted to determine the Tafel slopes of each electrode. Tafel slope is related to the kinetic of OER, involving rate and mechanism. The Tafel slopes are very similar for all electrodes calcined at different temperatures, except the G-CFO-500 electrode, which may be an indication of another reaction mechanism due to currently an unknown reason.

#### 3.1.4. Synthesis and Characterization of Mesoporous Calcium Iron Oxide Thin Films Using Chloride Precursors

The solutions using chloride precursors ( $\text{FeCl}_2$  and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) and two surfactants (namely, 10-lauryl ether ( $\text{C}_{12}\text{EO}_{10}$ ) as a non-ionic surfactant and CTAB as a charged surfactant) were prepared to investigate the formation of LLC mesophases and the effect of aging LLCMs. The solution is unstable and gives precipitates (within one day) without the addition of HCl, but the addition of 0.5 g HCl stabilizes the solution (clear solution) for up to several days. The formation of LLC mesophases was investigated by spin-coating and drop-casting of the above solutions. The presence of a diffraction line at around  $2.06^\circ$  and a shoulder at around  $1.95^\circ$  ( $2\theta$ ) indicates the formation of LLCMs. The sharp line observed from the spin-coated sample at about  $2.06^\circ$  becomes a broader line after 5-10 minutes of aging the LLCMs. But, in the case of a drop-casted sample, the same

diffraction line remains a bit longer than spin-coated. The diffraction lines were observed at 2.28, 2.54, 2.78, 3.06, and 4.14°, 2 $\theta$ . The unit cell parameters calculated using an orthorhombic d-spacing system are 52.2, 57.7, and 85.3 Å for a, b, and c, respectively. The parameters are almost similar to those mentioned in the water case. Figure 3.22 (d) shows that there is no salt crystallization during the one-hour aging of the gel sample. The mesophases were also analyzed after five days of aging the solution. It is observed that with aging, the diffraction line appears at a slightly higher angle, indicating a decrease in d-spacing, see Figure 3.22.

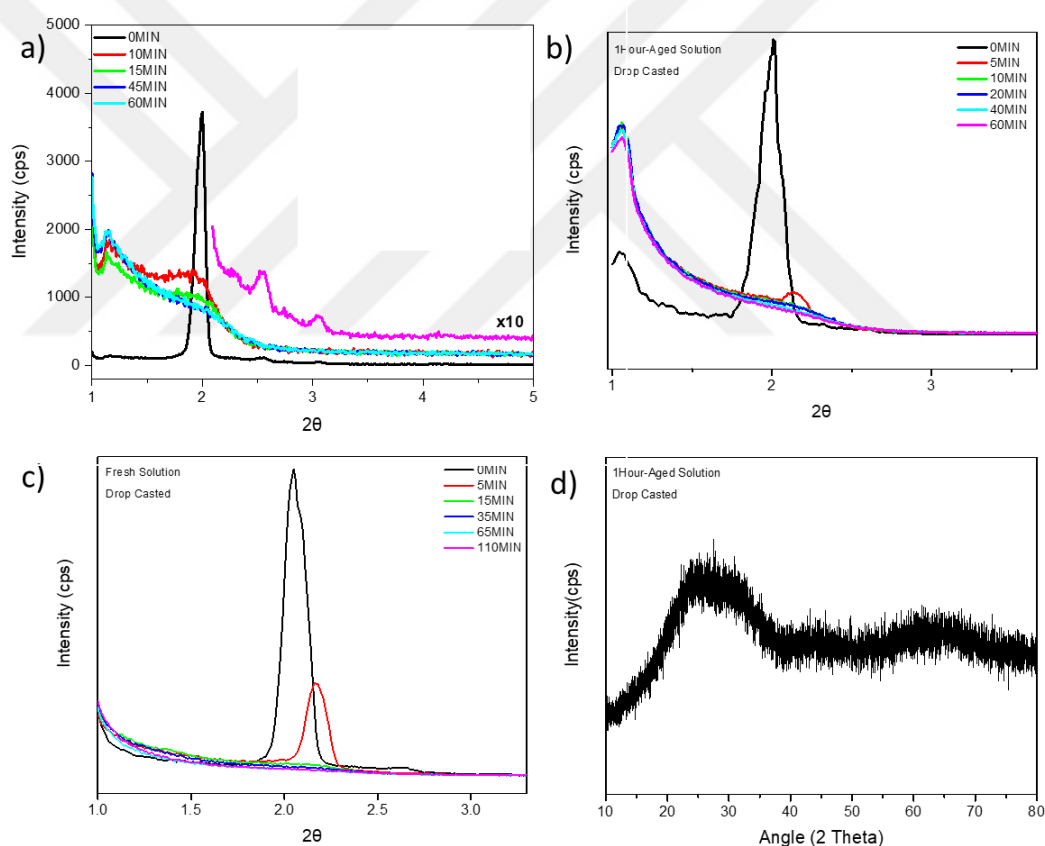


**Figure 3. 22.** Small-angle XRD patterns for LLCs (Ca:Fe, 2:4) using chloride precursors (a) from a spin-coated fresh solution, (b) 1-hour aged and drop-casted solution, (c) drop-casted fresh solution, and (d) high angle XRD pattern of drop-casted after 1-hour aging the solution.

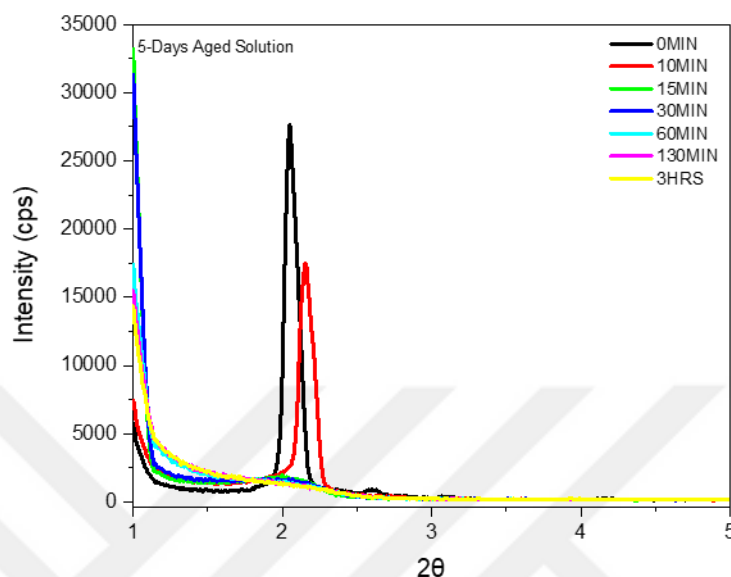


**Figure 3. 23.** Small-angle XRD patterns for LLCMs (Ca:Fe 2:4), prepared by using the 5-day aged solution.

Figure 3.23 shows that even after five days, the solution coated on a glass slide still exhibits diffraction, indicating the stability of the solution phase. Furthermore, the broad diffraction pattern suggests that the mesophase formation on the glass slide is stable for at least 3 hours. However, it is noteworthy that after 5 minutes, there is a shift in the peak of the mesophase towards a higher angle, indicating a reduction in d-spacing.

Figure 3.24 shows a set of temperature-dependent high-angle XRD patterns. Interestingly, there is no or less formation of carbonates in the synthesis of CFO using chloride precursors. Also, it shows that the material is crystalline even at 300 °C, indicating iron oxide. In this case, the CFO formation goes through an iron oxide route. But, in the case of CFO, prepared using nitrate precursors, it followed a formation of CFO through the route of amorphous calcium carbonate; as explained earlier, it is difficult to differentiate between the XRD patterns of iron oxide and CFO. Iron oxide formation starts to convert at lower temperatures into CFO as the primary phase, and a trace of  $\text{CaFe}_2\text{O}_5$  forms at higher temperatures. Finally, most of the peaks at 800 °C are perfectly aligned with the

XRD pattern of  $\text{CaFe}_2\text{O}_4$  with a trace of iron oxide and  $\text{CaFe}_2\text{O}_5$  crystals. But still, at 800 °C calcined sample consists of some impurities such as  $\text{CaFe}_2\text{O}_5$  and some traces of  $\text{Fe}_2\text{O}_3$ .

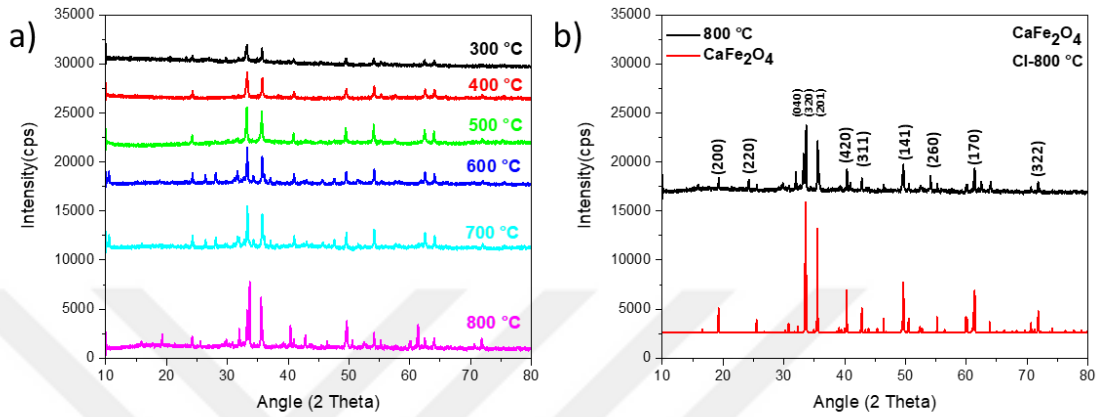


**Figure 3. 24.** Temperature dependent high angle XRD pattern of CFO powders

Scherer's equation is used to calculate the crystal size. The crystal size is calculated using the line at 33.55° (2 $\theta$ ) line and tabulated in Table 3.3.

| Calcination Temperature | Crystal Size (nm) |
|-------------------------|-------------------|
| 300 °C                  | 25                |
| 400 °C                  | 27                |
| 500 °C                  | 39                |
| 600 °C                  | 50                |
| 700 °C                  | 54                |
| 800 °C                  | 45                |

**Table 3. 3.** Crystal size (nm) at different calcination temperatures (Ca:Fe, 2:4).

Figure 3.25 displays the SEM images of the sample calcined at 300 °C. The images show flake-like particles. High-resolution transmission electron microscopy (HR-TEM) reveals the porous structure of CFO at 300 °C, which is semi-crystalline. The images of the sample calcined at 300 °C display sponge-like porosity; however, with further annealing of the sample, the porous structure collapse, and a particle-like morphology is observed, see Figure 3.26 (d). The lattice fringes in Figure 3.26 (c) indicate that those particles are highly crystalline.



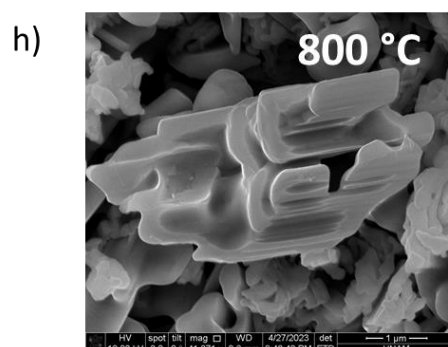
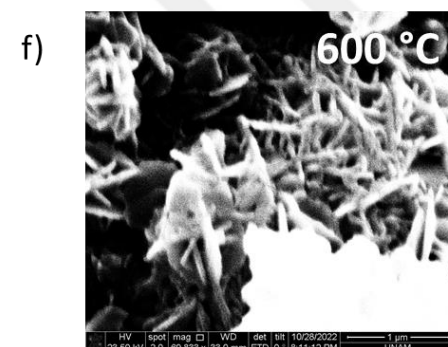
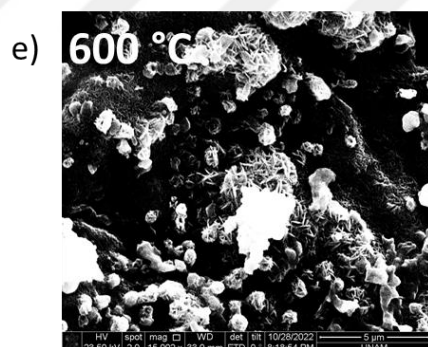
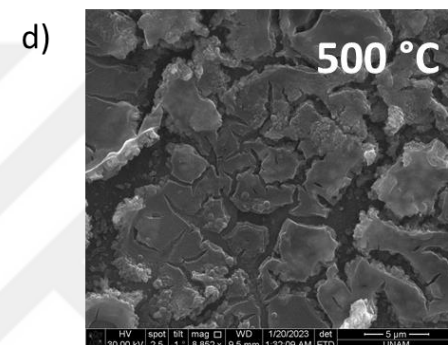
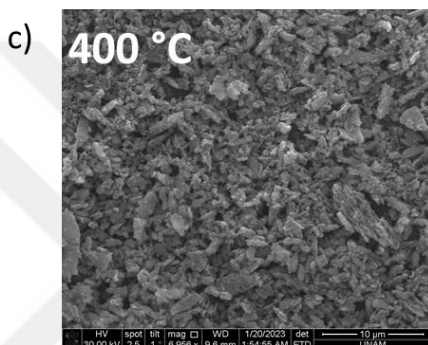
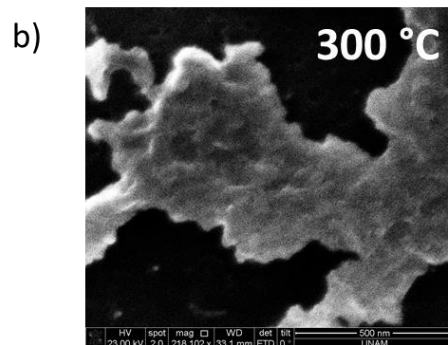
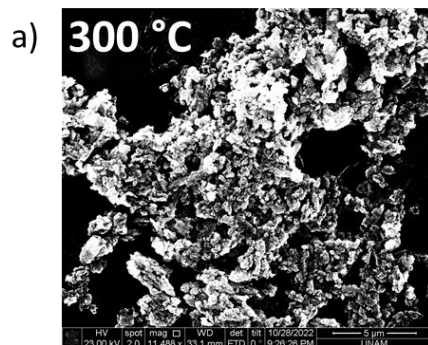


**Figure 3. 25.** SEM images of m-CFO-Cl-XXX samples prepared at various temperatures, including (a) and (b) at 300 °C with scale bars of 3  $\mu\text{m}$  and 500 nm, respectively; (c) at 400 °C with a scale bar of 10  $\mu\text{m}$ ; (d) at 500 °C with a scale bar of 5  $\mu\text{m}$ ; (e) and (f) at 600 °C with scale bars of 5  $\mu\text{m}$  and 1  $\mu\text{m}$ , respectively; and (g) and (h) at 800 °C with scale bars of 4  $\mu\text{m}$  and 1  $\mu\text{m}$ , respectively.

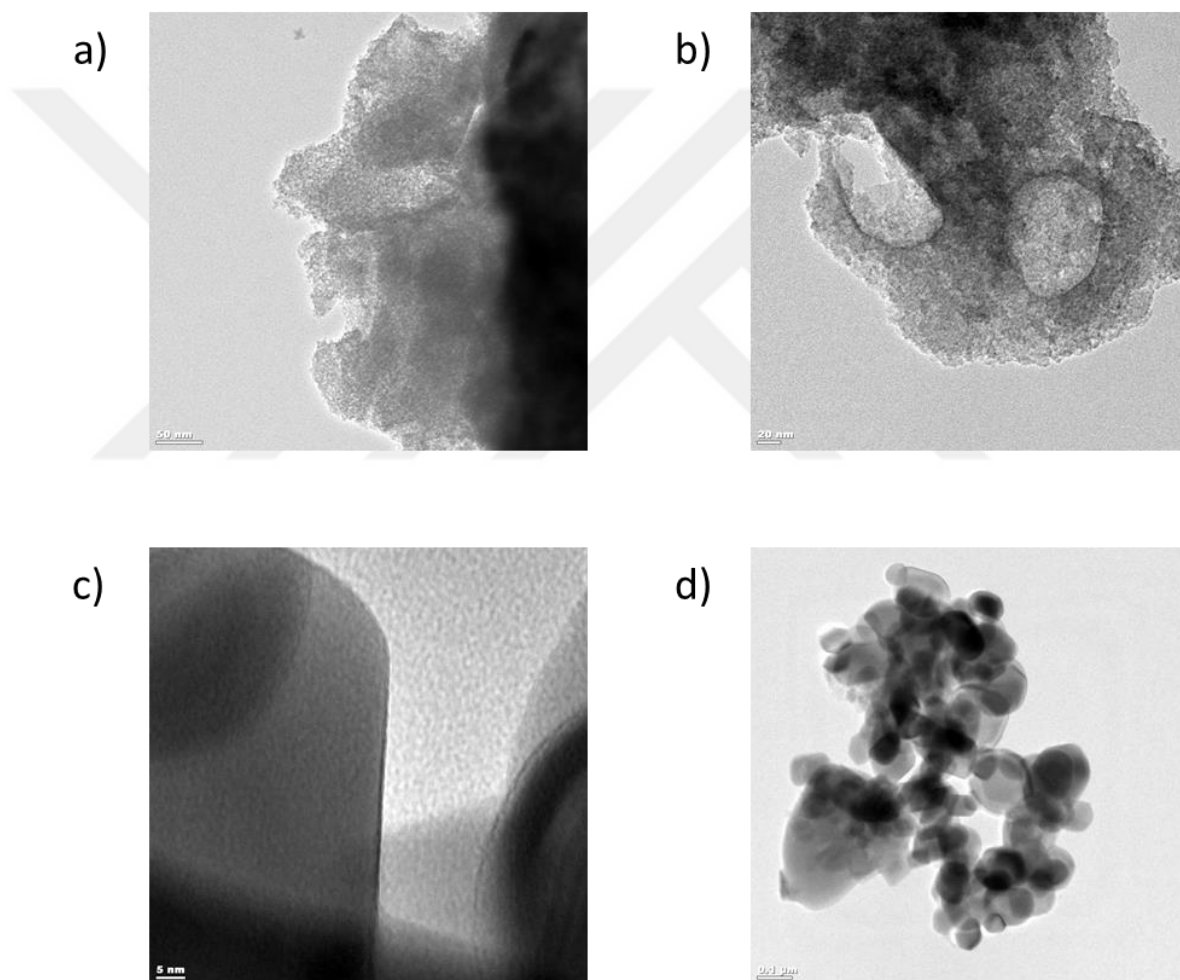


**Figure 3. 26.** HR-TEM images of the samples, calcined at (a, b) 300°C and (c, d) 800 °C.

Figure 4.6 displays the  $\text{N}_2$  (77K) adsorption-desorption isotherms for the powder, obtained by scraping from glass slides at 300 °C. Surprisingly, the resulting powder shows a very low surface area of only 5  $\text{m}^2/\text{g}$ , despite the relatively low calcination temperature. This finding contrasts the TEM images, which revealed a porous structure of the CFO prepared

using chloride precursors. But consistent with the XRD data that display sharp diffraction lines due to relatively large crystals, check Table 4.1. Therefore, the contrasts in the TEM images could be misleading, or a small fraction of the sample is porous, but the rest is nanocrystalline with a small surface area.

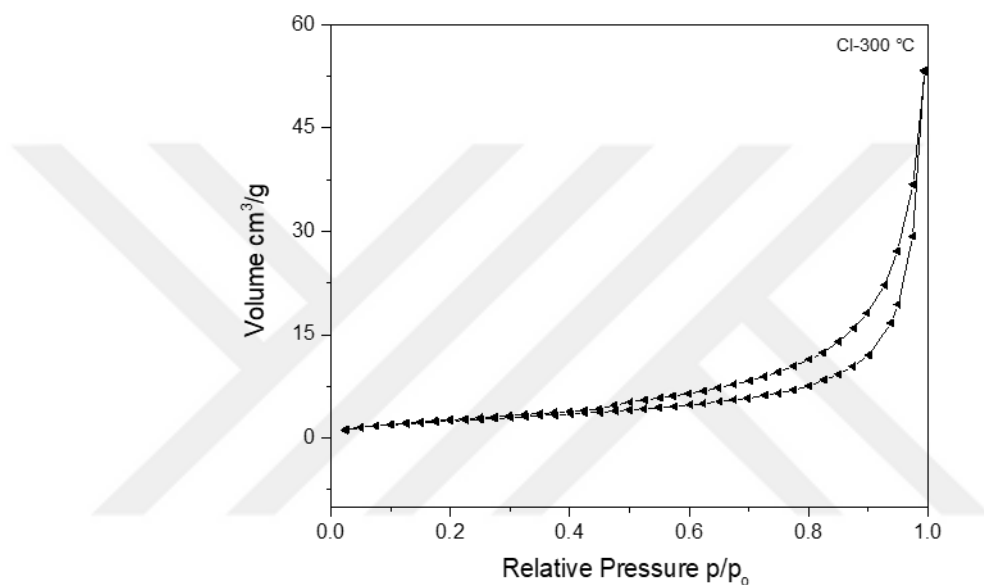


**Figure 3. 27.** N<sub>2</sub> (77K) adsorption-desorption isotherm of the powder, calcined at 300 °C.

### 3.1.5. Mesoporous G-CFO-Cl-XXX Thin Films as Electrocatalyst for Oxygen Evolution Reaction (OER)

Similarly, the solutions were coated over graphite rods by dip-coating method and calcined to prepared electrodes at each calcination temperature (decoded as G-CFO-Cl-XXX, where G stands for graphite rod, CFO is CaFe<sub>2</sub>O<sub>4</sub>, Cl represents chloride precursors, and XXX is the calcination temperature). The electrochemical experiments were also performed to analyze the electrochemical performance of G-CFO-Cl-XXX electrodes in OER.

At first, cyclic voltammetry (100 cycles) was used to elucidate the stability of the electrode at each temperature. The potential window chosen for the CVs is -0.1 V-1.5 V versus normal hydrogen electrodes (NHE).

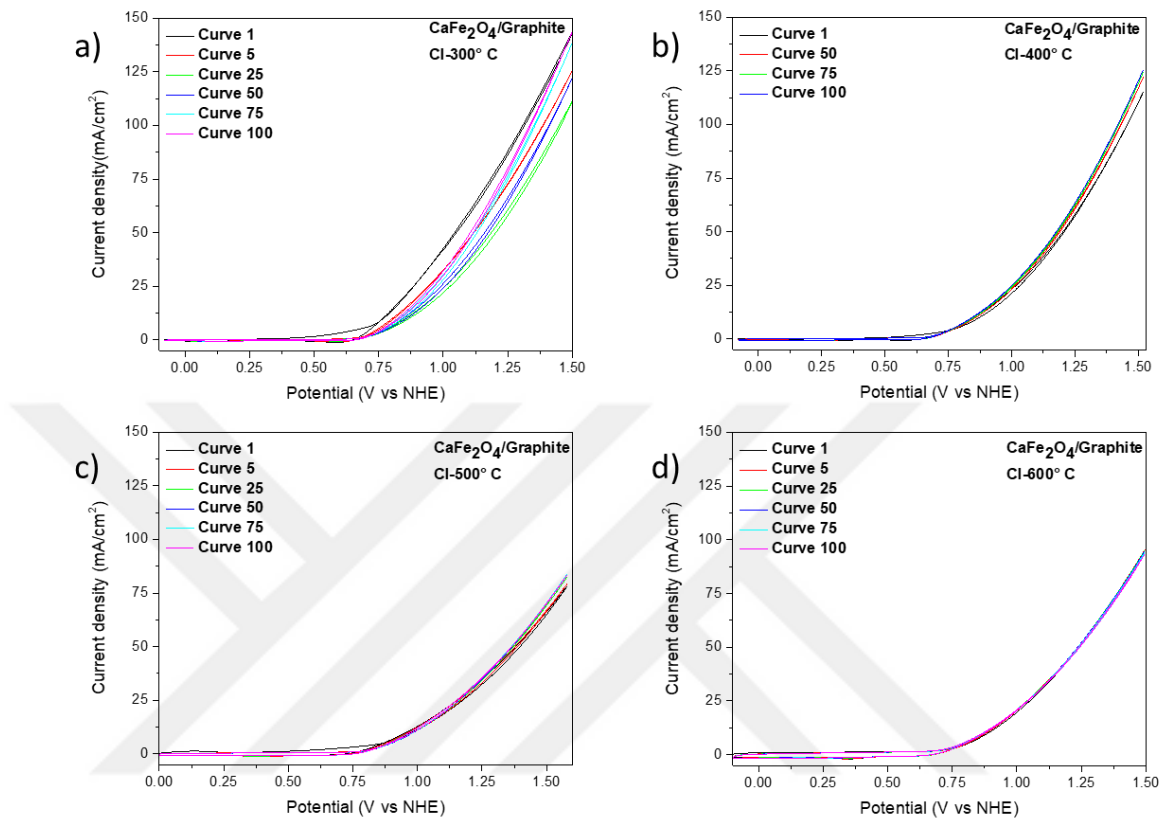


**Figure 3. 28.** Multiple CVs of G-CFO-Cl electrodes, calcined at **(a)** 300 °C **(b)** 400 °C **(c)** 500 °C, and **(d)** 600 °C.

Figure 3.28 (a) shows the CVs of G-CFO-Cl-300 electrodes. The current density decreases till the 25<sup>th</sup> cycle, and after that, it improves with usage; as shown up to the 100<sup>th</sup> cycle, it comes back to the same current density as it was in the 1<sup>st</sup> cycle. The current density continuously improves in the G-CFO-Cl-400 and G-CFO-Cl-500 electrodes. For the G-CFO-Cl-600 electrode (see Figure 3.28(d)), there is a slight decrease in current density after the 100<sup>th</sup> cycle. These experiments not only show the stability of the electrodes but also show an improved electrode performance.

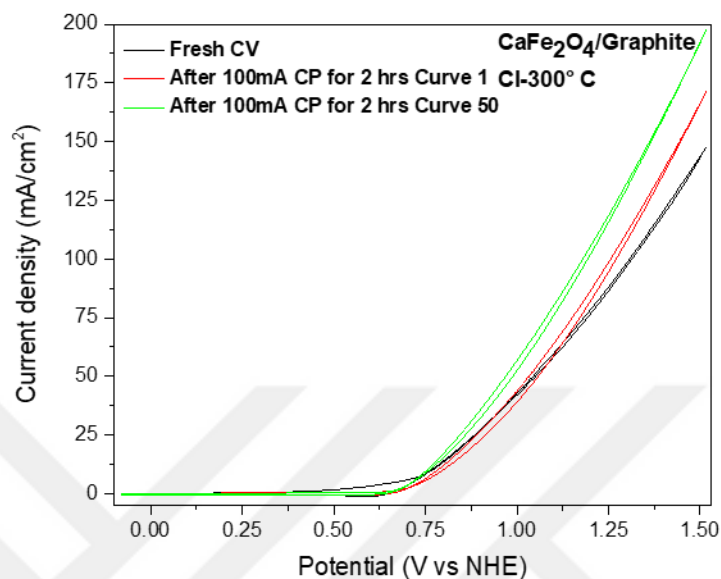


**Figure 3. 29.** CVs indicating the improved performance of electrodes with usage.

We observed that even after using the electrodes in harsh conditions, the electrode performance gets better. For one G-CFO-Cl-300 electrode, 100 CVs were recorded from the fresh electrode, then the chronopotentiometry experiment was conducted at 100 mA for 2 hours, and then again, 50 CVs were recorded. After that, 1st CV, the CV after the CP experiment, and a CV after 50 cycles were compared in Figure 3.29. It was noticed that the current density at the water oxidation side is increasing with usage.

To calculate the over-potentials at 1, 10, and 100 mA cm<sup>-2</sup> current densities, a series of chronopotentiometry (CP) experiments were also performed. At each current density, experiments were conducted for two hours, and the last point was recorded as a value of overpotential (extra voltage required for OER).

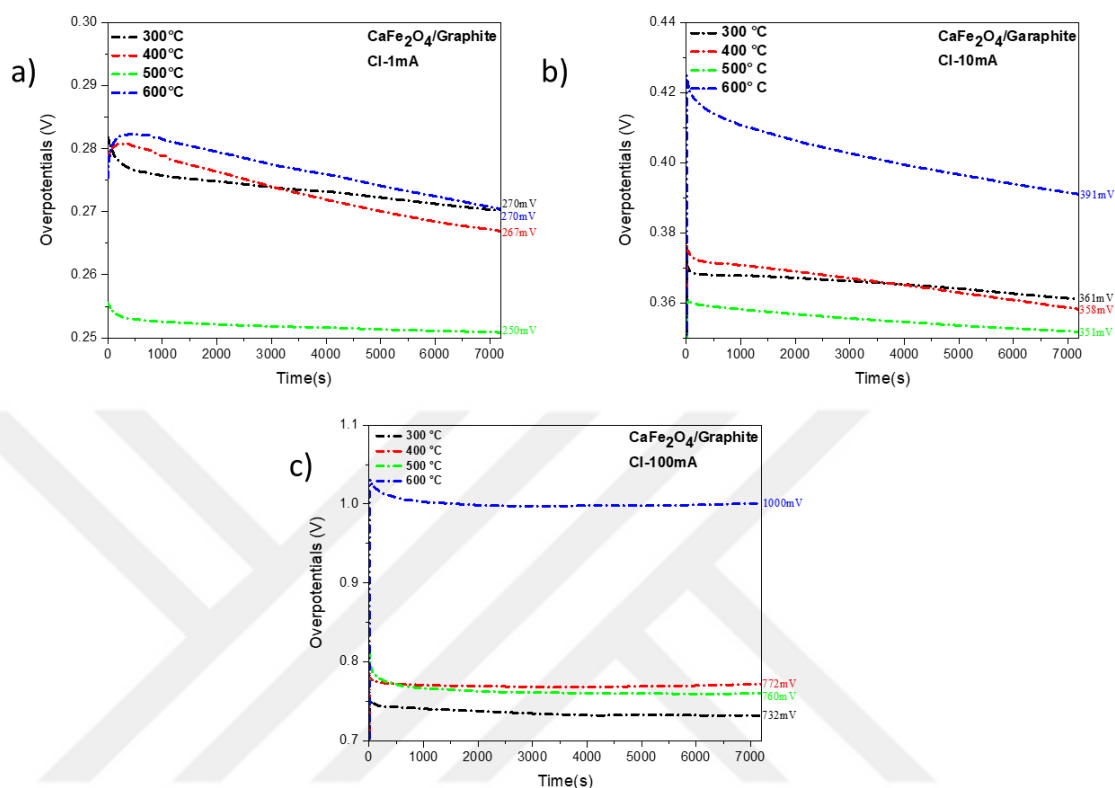


**Figure 3. 30.** Overpotentials versus time plots, chronopotentiometry (CP) of all electrodes, calcined at various temperatures at (a) 1mA cm<sup>-2</sup>, (b) 10 mA cm<sup>-2</sup>, and (c) at 100 mA cm<sup>-2</sup> current densities for 2 hours.

The figure shows that overpotentials at each current density almost have the same values except the G-CFO-CI-600 electrode, which shows a bit high overpotentials. In the case of 1mA cm<sup>-2</sup> and 10 mA cm<sup>-2</sup>, overpotentials decay with usage, indicating an improved electrode performance. The overpotentials are almost similar at the 100 mA cm<sup>-2</sup> current density, indicating good electrode stability.

The comparison of all the electrodes, calcined at different temperatures, is given in Figure 3.31. These data show that the performance of the electrodes is improved even with usage in harsh conditions (almost 10-12 hours usage at higher current densities).

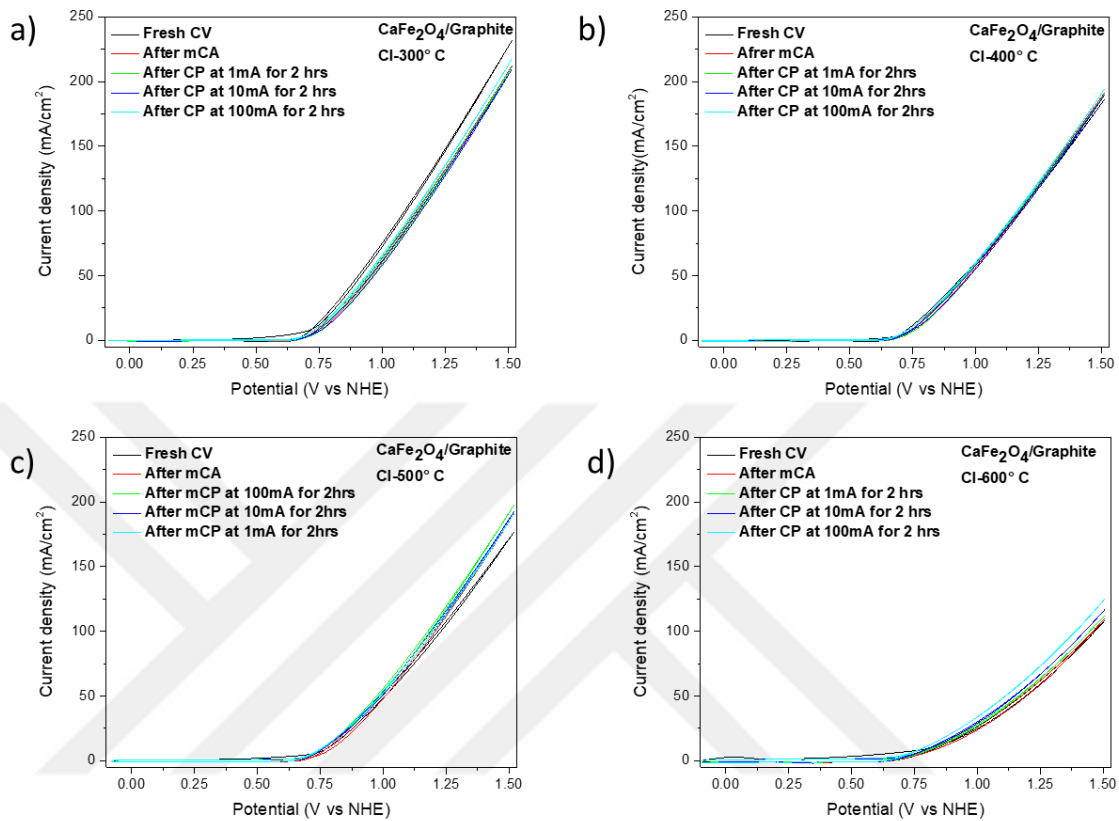


**Figure 3. 31.** Comparison of CVs after each experiment for the analysis of performance of electrodes, calcined at **(a)** 300 °C **(b)** 400 °C **(c)** 500 °C, and **(d)** 600 °C .

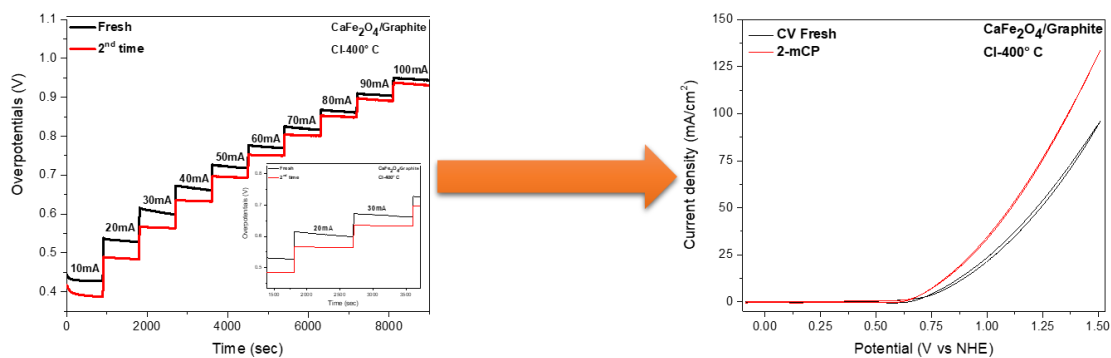


**Figure 3. 32.** Plot of chronopotentiometry and cyclic voltammetry elucidating improved performance of G-CFO-Cl-400 electrode with usage.

In order to further demonstrate the enhanced performance of calcium iron oxide-coated (G-CFO-CI-400) electrodes, a multi-step chronopotentiometry (m-CP) analysis was conducted, with cyclic voltammograms (CVs) recorded both before and after two m-CP measurements. The m-CP data revealed a significant increase in current density, from 90 mA to almost 140 mA, indicating a marked improvement in electrode performance. The second m-CP measurement demonstrated even lower overpotentials for the same electrode, as shown in Figure 3.32.

The first m-CP measurement showed that the overpotentials were stable and decreased with time, suggesting that the electrodes are highly durable, conductive, and suitable for harsh conditions (Figure 3.32, inset). Furthermore, the second m-CP measurement revealed that the decrease in overpotentials in each step was not as pronounced as in the first run, suggesting that the material coated on the electrode was no longer becoming activated. It should also be noted that the jump from 10 to 20 mA was more significant than the jump from 90 to 100 mA in both runs, which may indicate that the electrodes exhibit more excellent activity at higher current densities.

Multistep chronoamperometry experiments are conducted to determine the Tafel slopes of each electrode. The Tafel slope linearly increases from 47 to 72 mV/dec going from 300 to 600 °C. Increasing Tafel slopes show the OER mechanism change at higher temperatures. It is likely that the catalytic sides on the electrode surface change with heating at higher temperatures. It can be the most probable explanation of the conversion of iron oxide to CFO from low temperature (300 °C) to high temperature (600-800 °C).

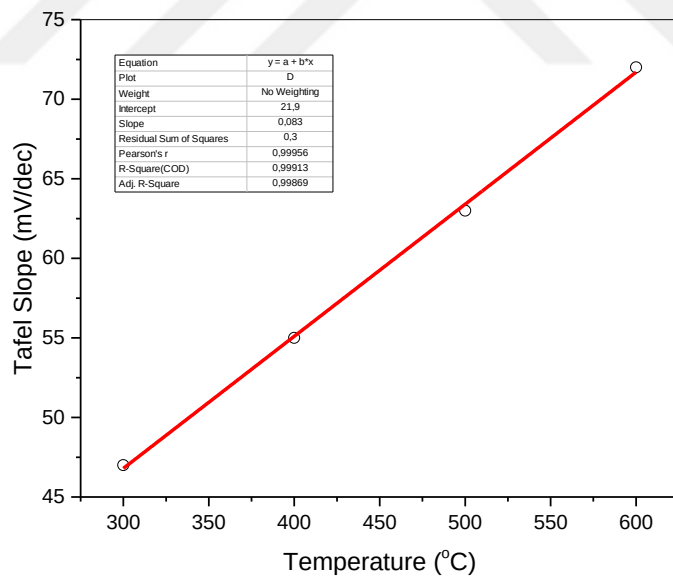
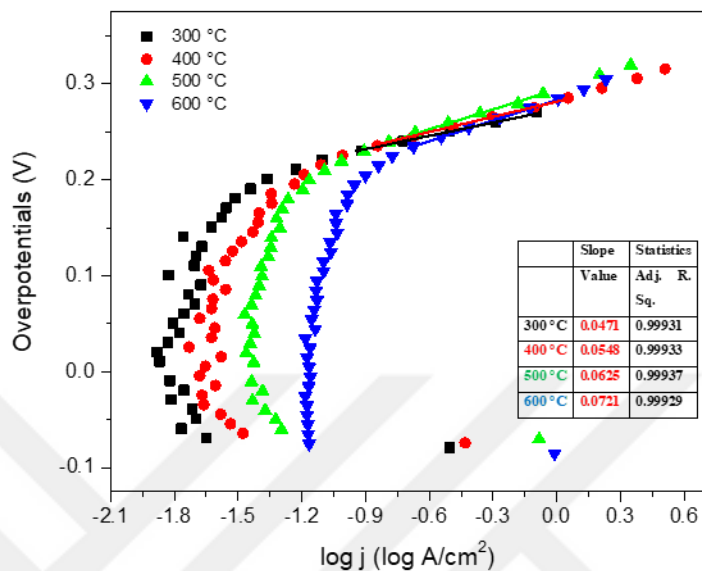


**Figure 3. 33.** Temperature-dependent Tafel slopes of the G-CFO-Cl-XXX electrodes.

To confirm the stability of the electrode, an additional experiment was conducted. In this experiment, a constant current is applied to the working electrode for 30 minutes, then the

Tafel slope is measured. After every step, the value of the Tafel slope is almost similar, indicating the electrode's stability even under the harsh conditions of the current applied.

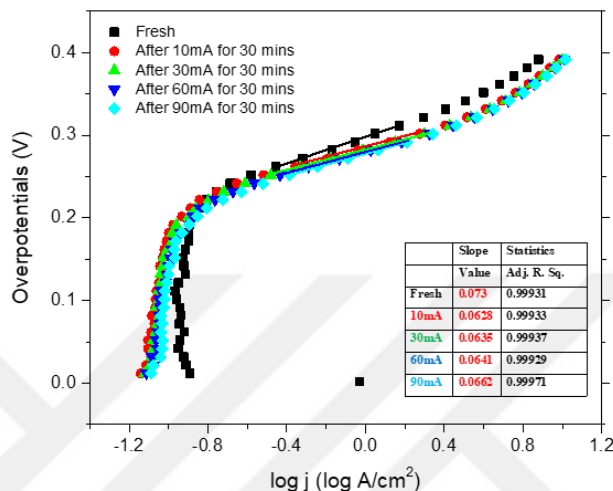


**Figure 3. 34.** Tafel plots after each current density to ensure the stability of G-CFO-Cl-600 electrodes.

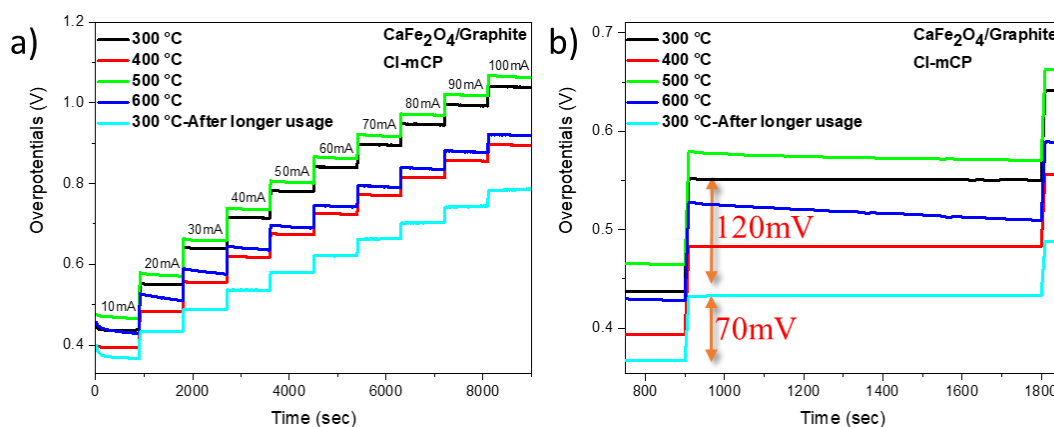


**Figure 3. 35.** Plot of multistep chronopotentiometry (m-CP) of all the electrodes at various current densities, ranging from 10 to 100 mA cm<sup>-2</sup>. Each step took 15 minutes.

Multiple-step chronopotentiometry (m-CP) experiments were performed to measure the overpotentials at different current densities. The duration of each step was 15 minutes,

and it was noted that they did not exhibit any significant temperature dependence. To investigate the effect of prolonged usage on electrode performance, an electrode calcined at 300 °C was subjected to harsh conditions, namely 100 cyclic voltammograms (CVs) and constant potential (CP) at 100 mA for 2 hours, followed by m-CP measurements to compare its efficiency with that of a fresh electrode. The results indicate that the electrode's performance improved after prolonged usage, which is consistent with previous observations of increased activity in electrodes prepared using chloride precursors due to decreased resistance and increased conductivity. Multistep chronopotentiometry was used to elucidate this phenomenon further, as shown in Figure 3.35 (b), where the m-CP for the 300 °C electrode (black curve) required an overpotential of 120 mV to go from 10 mA to 20 mA. In contrast, when the same electrode (sky-blue curve) was subjected to several hours of electrochemical experiments before the m-CP measurement, it exhibited enhanced activity and conductivity, as evidenced by a reduced resistance, and only required an overpotential of 70 mV to achieve the same current density.

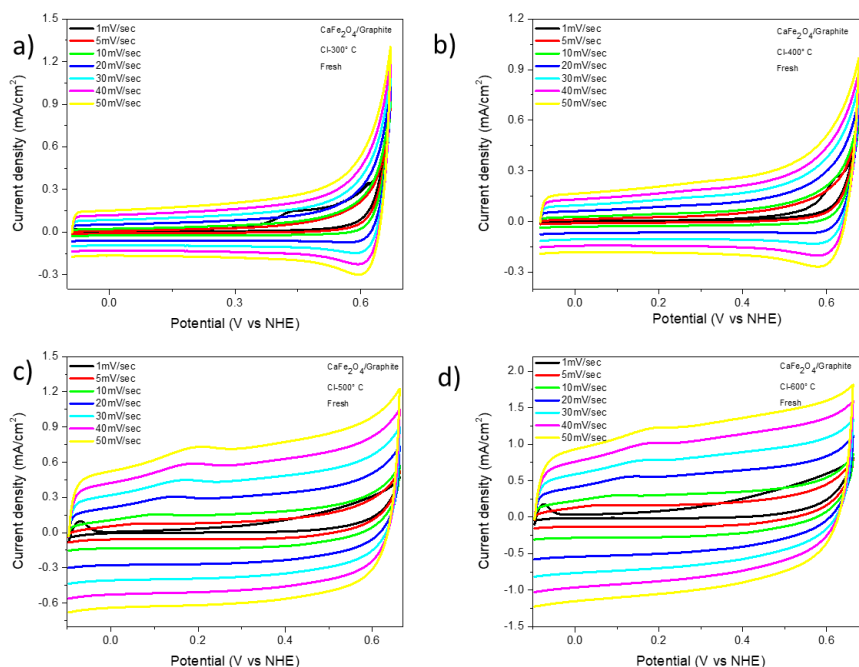


**Figure 3. 36.** Scan rate-dependent CVs of the G-CFO-Cl electrodes, calcined at **(a)** 300 °C **(b)** 400 °C **(c)** 500 °C , and **(d)** 600 °C.

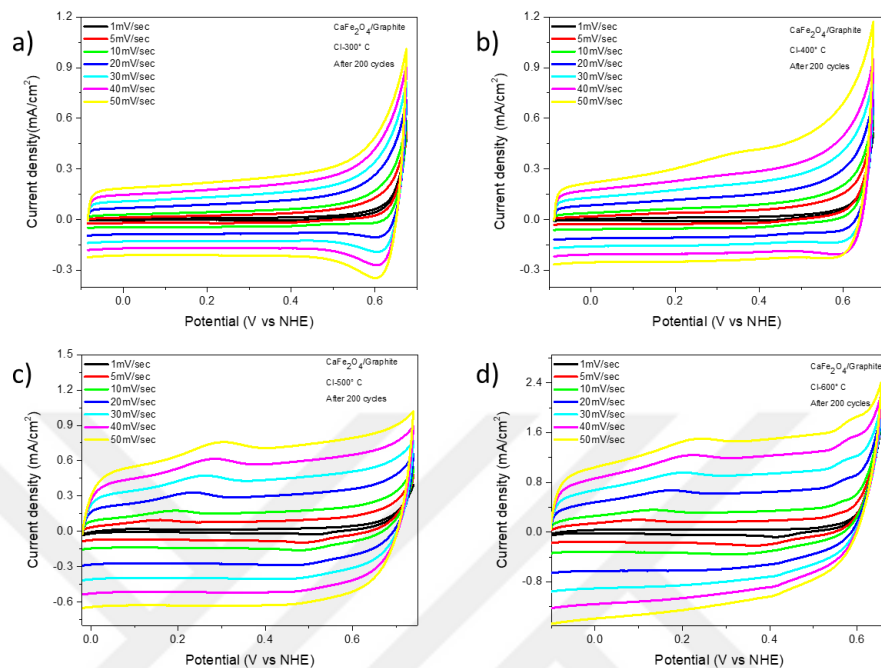


**Figure 3. 37.** Scan rate-dependent CVs of the G-CFO-Cl electrodes (after 200 cycles), calcined at **(a)** 300 °C **(b)** 400 °C **(c)** 500 °C, and **(d)** 600 °C.

The scan rate-dependent experiments are also conducted for each temperature to evaluate whether the OER is a diffusion or surface-controlled reaction. Similarly, a random potential of 0.48 V was chosen for all the plots at this potential current value against each scan rate. The log current density ( $\log I \text{ mA cm}^{-2}$ ) versus log scan rate ( $\log \nu$ ) is plotted, and the linear fit gives a slope for each experiment. The slope value is around 0.73 for the G-CFO-Cl-300 and G-CFO-Cl-400 electrodes, indicating the OER occurs by both processes, i.e., diffusion and surface controlled. But, for the higher temperatures, this value rose, showing more surface-controlled reactions than diffusion. It may be because of less surface area at higher temperatures or because pores are no longer accessible to charge carriers. The same scan rate-dependent experiments were also repeated after 200 cycles of cyclic voltammetry (-0.1-0.66V) to investigate the effect on diffusion after surface usage. The increase in slope values shows that the OER are surface controlled after surface usage. They are not any more diffusion controlled.

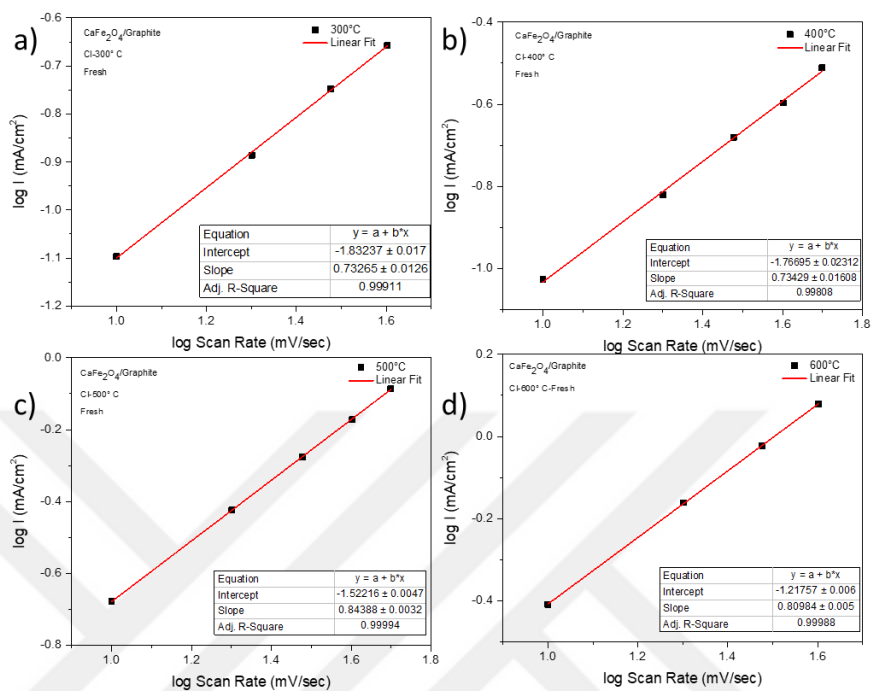


**Figure 3. 38.** Plot of log current density ( $\log I$  mA cm<sup>-2</sup>) versus  $\log$  scan rate ( $\log v$ ) for different fresh electrodes, calcined at (a) 300 °C (b) 400 °C (c) 500 °C, and (d) 600 °C.

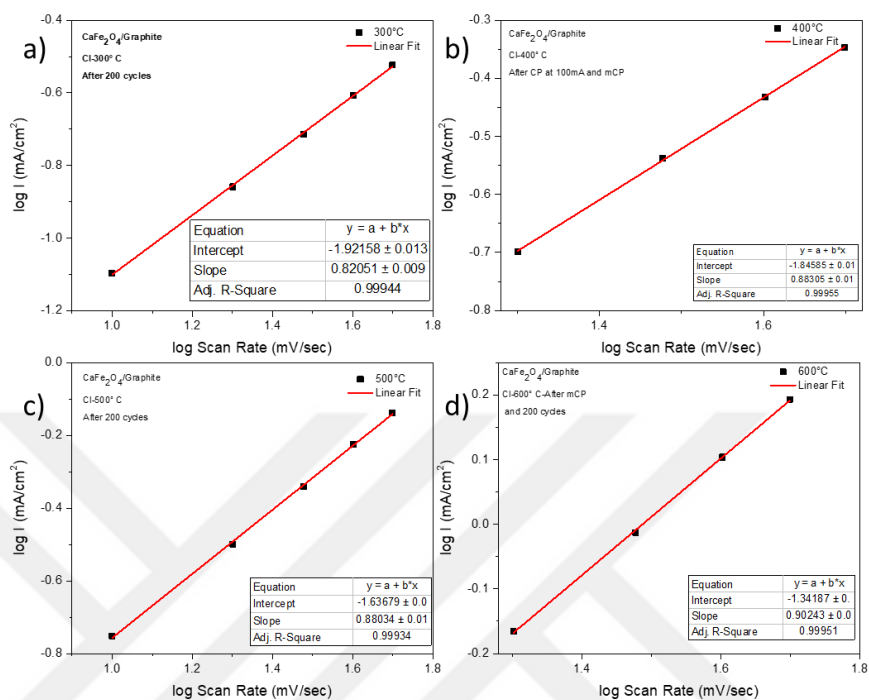


**Figure 3. 39.** Plot of log current density ( $\log I$   $\text{mA cm}^{-2}$ ) versus log scan rate ( $\log v$ ) for different electrodes (after 200 cycles), calcined at **(a)** 300 °C **(b)** 400 °C **(c)** 500 °C, and **(d)** 600 °C.

### 3.1.6. Synthesis and Characterization of Mesoporous Calcium Iron Oxide Thin Films Using Ethanol as Solvent:

We also prepared  $\text{CaFe}_2\text{O}_4$  using ethanol as a solvent, using both mole ratios (2:4 and 3:6, Ca:Fe), to elucidate the effect of solvent and concentration of metal salts on particle size and morphology. The table below shows the compositions used for the synthesis of the CFO.

| Ca : Fe<br>mole<br>ratio | $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$<br>(g) | $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$<br>(g) | CTAB<br>(g) | $\text{C}_{12}\text{EO}_{10}$<br>(g) | Ethanol<br>(g) |
|--------------------------|-------------------------------------------------------------|-------------------------------------------------------------|-------------|--------------------------------------|----------------|
| 2:4                      | 1.2721                                                      | 0.3738                                                      | 0.287       | 0.5                                  | 5              |
| 3:6                      | 1.9149                                                      | 0.5596                                                      | 0.287       | 0.5                                  | 5              |

**Table 3. 4.** Amounts of chemicals for  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ - $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ - $\text{C}_{12}\text{EO}_{10}$ -CTAB-Ethanol

Similarly, the surfactant is dissolved first in solvent and stirred for a while to get a clear solution. After that, salts are added and stirred for 5 minutes to obtain a clear solution. As described earlier, this solution was coated on glass slides and graphite rods for further characterization. After coating on a glass slide, an LLC mesophase forms immediately on the surface of the glass slide.

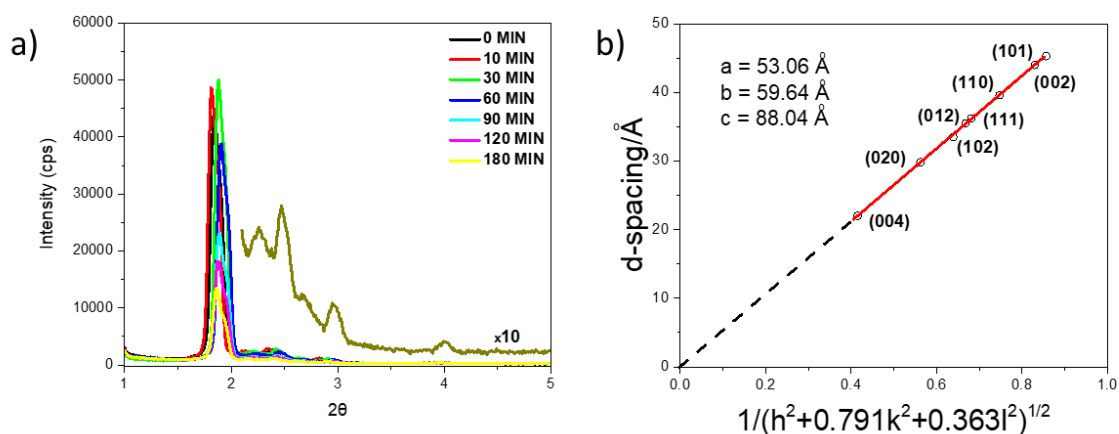


**Figure 3. 40.** Small-angle XRD patterns for LLCMs (Ca:Fe, 2:4) for a fresh solution

Clear solutions of nitrate precursors ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ - $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ ) and two surfactants (10-lauryl ether ( $\text{C}_{12}\text{EO}_{10}$ ) as a non-ionic surfactant and CTAB as a charged surfactant) were also prepared using ethanol to investigate the formation of the lyotropic liquid crystalline mesophase (LLCM) and effect of aging of the solution on the LLCMs. The formation of LLCMs was investigated by coating the solution using spin-coating and drop-casting methods. Figure 3.40. shows a set of time-dependent small-angle XRD patterns of a 2:4 mole ratio after gelation. As shown in the XRD pattern in Figure 3.40., the line at around  $1.84^\circ$  indicates the formation of LLCMs for a 2:4 mole ratio. Other almost eight diffraction lines suggest that the mesophase is highly ordered. For the 3:6 mole ratio, the diffraction line at around  $1.94^\circ$ ,  $2\theta$ , in Figure 3.41, indicates the formation of LLCMs. Similarly, the other many diffraction lines ensure the highly ordered and oriented mesophase formation. In the case of a 2:4 mole ratio, the unit cell parameters calculated using an orthorhombic d-spacing system are 53.1, 59.6, and 88.0 Å for a, b, and c, respectively (almost 12% distortion). Similarly, in the case of, all the lines are slightly shifted towards a higher angle, indicating the decrease in d-spacing. The unit cell parameters calculated using an orthorhombic d-spacing system are 49.1, 57.7, and 86.6 Å for a, b, and c, respectively. It may indicate the enhanced polymerization of iron species in more salt-concentrated LLC mesophases. All the diffraction lines are indexed according to an orthorhombic system, and a linear plot ensures the correct assigned hkl values.

As shown earlier in this thesis, the mesophase is hexagonal if water is used as the solvent. Similarly, in the case of a 2:4 mole ratio from ethanol solution, we observed the formation of a hexagonal phase with a fan texture under POM, see Figure 3.42 (e and f). Interestingly, using ethanol as the solvent, the mesophase forms with smaller domains compared to the water sample. In the 3:6 mole ratio, it is hard to recognize the formation of any texture, but after 2 hours, some features start to grow, an unknown structure, and the phase is considered to be cubic, see Figure 3.42. (a to d). Also note that an aged solution, aged for 26 h, coated on a glass slide still displays the mesophase's main line but another intense line is observed at  $3.1^\circ$ ,  $2\theta$ . This line corresponds to CTAB that crystallizes out from the mesophase; likely, it has the same unknown origin (as observed in the POM images).

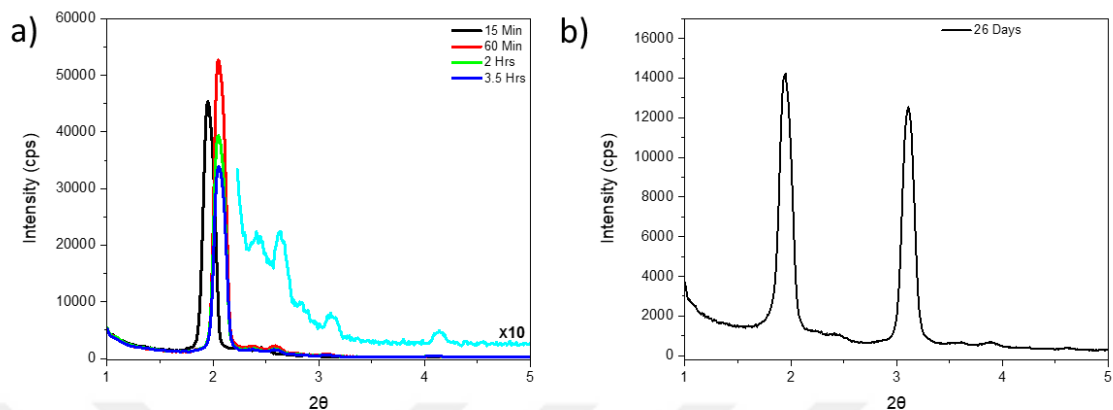


**Figure 3. 41.** Small-angle XRD patterns for LLCMs (Ca:Fe, 3:6) (a) for a fresh solution and (b) for a 26-days aged gel coated on glass slide.

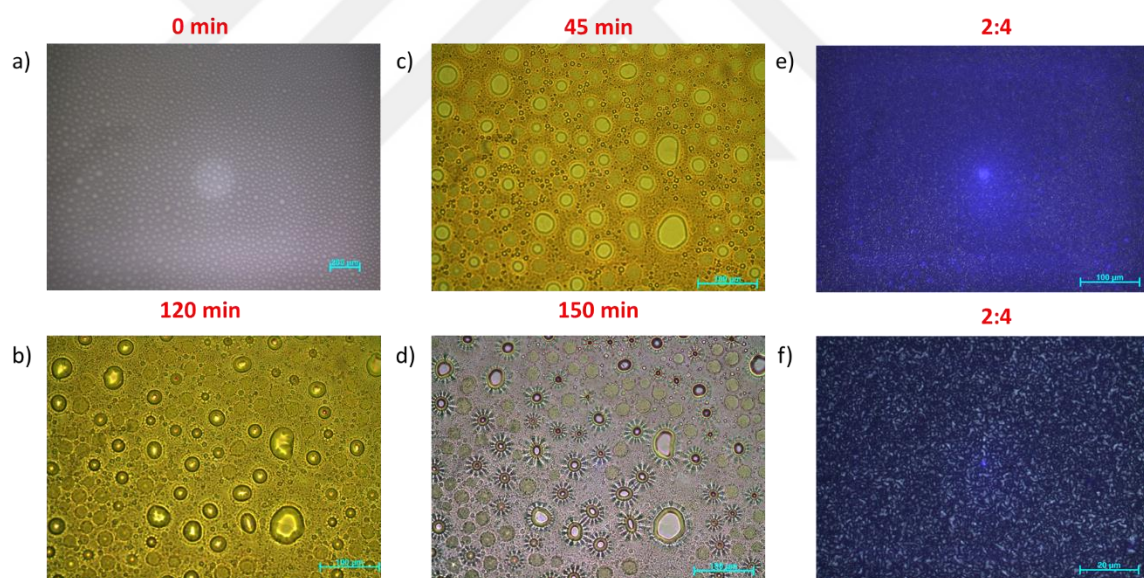


**Figure 3. 42.** POM images of LLCMs (Ca:Fe, 3:6) prepared by drop casting, including (a) through (d) at different time duration, and (e) and (f) for (Ca:Fe, 2:4)

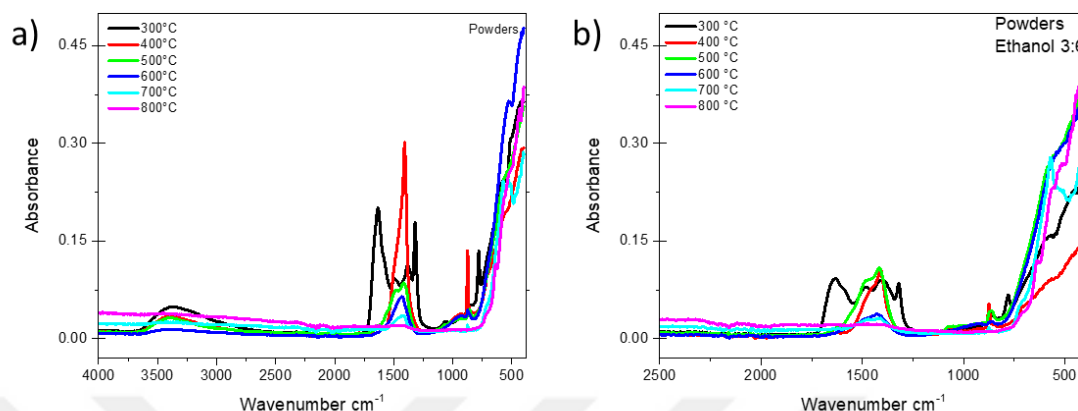


**Figure 3. 43.** ATR-FTIR spectra of CFO powders, calcined at different temperatures and Ca:Fe mole ratios of, (a) 2:4 (b) 3:6.

The formation of carbonates is unavoidable at low temperatures during the synthesis of calcium iron oxide; it does not matter which solvent or mole ratio is used. The appearance of carbonate or bicarbonates is always there. In both mole ratios, again at a lower temperature (at 300 °C), bicarbonates or surface carbonates are formed. At higher temperatures (above 300 °C), carbonates are formed; the peak at 1419  $\text{cm}^{-1}$  and 876  $\text{cm}^{-1}$  indicates carbonates' persistence till 600 °C, and then it starts to decompose. And diminishing the peak at 876  $\text{cm}^{-1}$  confirms a complete removal of carbonates and formation of CFO. But surprisingly, as shown in the figure, the formation of carbonates in powders prepared using the 3:6 mole ratio is lower than that of the 2:4 mole ratio.

Similarly, the glass slides were coated with the precursor solutions and aged for a while to obtain mesophases and then were subjected to calcination at 300 °C; after that, powders were scraped and further annealed at various higher temperatures. Wide-angle XRD patterns were recorded using these powders to obtain information about their structure and particle size. Figure 3.44 (a) shows the XRD patterns of the samples calcined at different temperatures. At lower temperatures, there is an amorphous phase of CFO, and subsequently, at 400 °C, crystalline carbonates are formed. We found that the carbonates have a different decomposition pathway to the formation of CFO if ethanol is used as the solvent. In this case, first carbonates decompose till 600 °C. Above 600 °C, a new phase

of  $\text{Ca}_2\text{Fe}_2\text{O}_5$  is observed; see Figure 3.44. Finally, this phase is converted into CFO at 800 °C. The red stars indicate the formation of  $\text{Ca}_2\text{Fe}_2\text{O}_5$  and their conversion of CFO. Similarly, in the case of the 3:6 mole ratio, see Figure 3.44 (b), heat treatment follows the same pattern. Still, calcium carbonate's crystallinity is prominent compared to all cases explained earlier. Figure 3.45 (a) and (b) show indexing of the XRD patterns of powder samples calcined at 800 °C using the reference CFO with a pdf card no. 00-032-0168. The porous materials are denoted as m-CFO-Eth-x:y-XXX (where m stands for mesoporous, CFO is  $\text{CaFe}_2\text{O}_4$ , x, and y are Ca and Fe surfactant mole ratio, and XXX is the calcination/annealing temperature in Celsius).

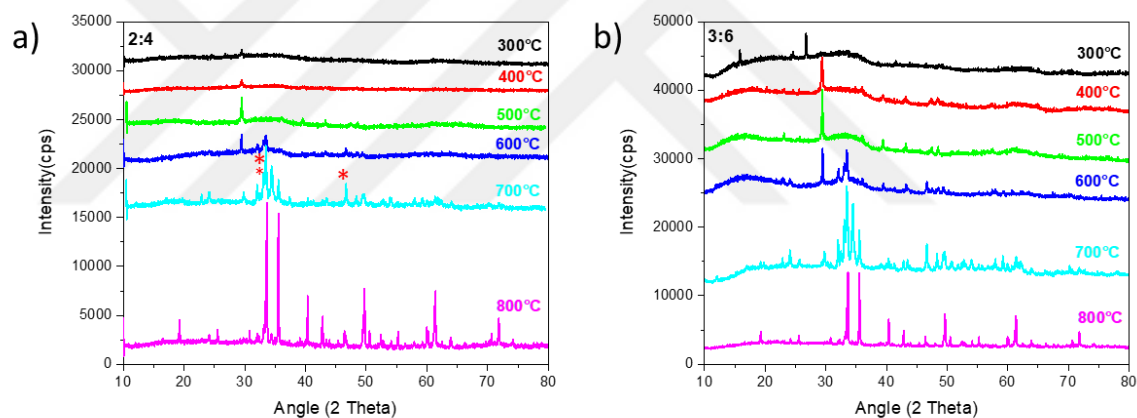


**Figure 3. 44.** Temperature-dependent high angle XRD pattern of CFO powders (a) m-CFO-Eth-2:4-XXX (b) m-CFO-Eth-3:6-XXX

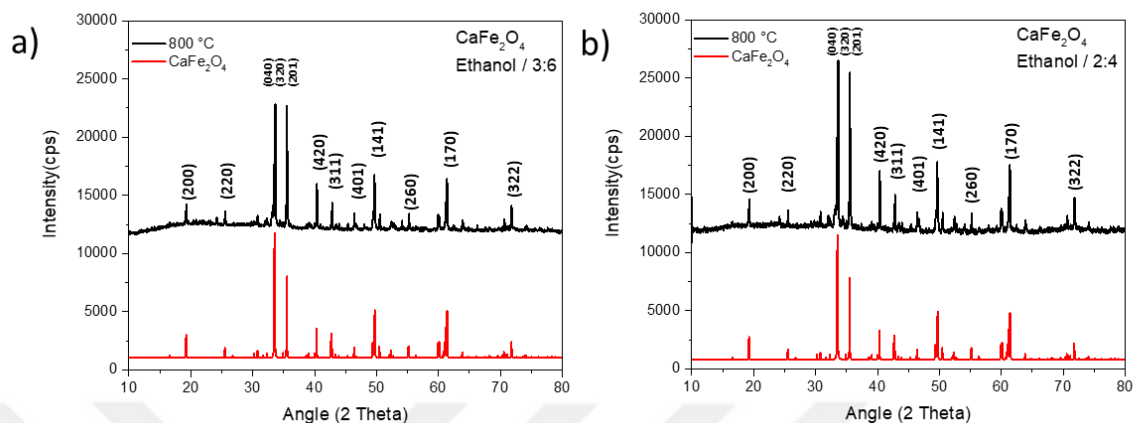


**Figure 3. 45.** Wide-angle XRD patterns of (a) m-CFO-Eth-3:6-800 (b) m-CFO-Eth-2:4-800

To calculate the surface area and obtain information about the pore size distribution of CFO powders prepared using ethanol (for both mole ratios 2:4 and 3:6) as a solvent and calcined at various temperatures, we collected N<sub>2</sub> adsorption-desorption isotherms for all samples. We observed that ethanol plays a crucial role in retaining the porous structure; therefore, the surface area does not drop drastically with the increase in temperature. To illustrate this, it can be seen in Table 3.5 that, in both mole ratios, the surface area at 300 °C is about 145 m<sup>2</sup>/g, and even at 600 °C, where pores can be damaged, we still obtained a surface area of around 45 m<sup>2</sup>/g. As mentioned earlier, pore size expands with the increased calcination temperature; still, using ethanol as a solvent could retain a porous structure with a surface area of 7 m<sup>2</sup>/g for an 800 °C calcined sample (highly crystalline

pore walls). Figure 3.46. (c) and (d) demonstrates the expansion of pores with the increased calcination temperatures.

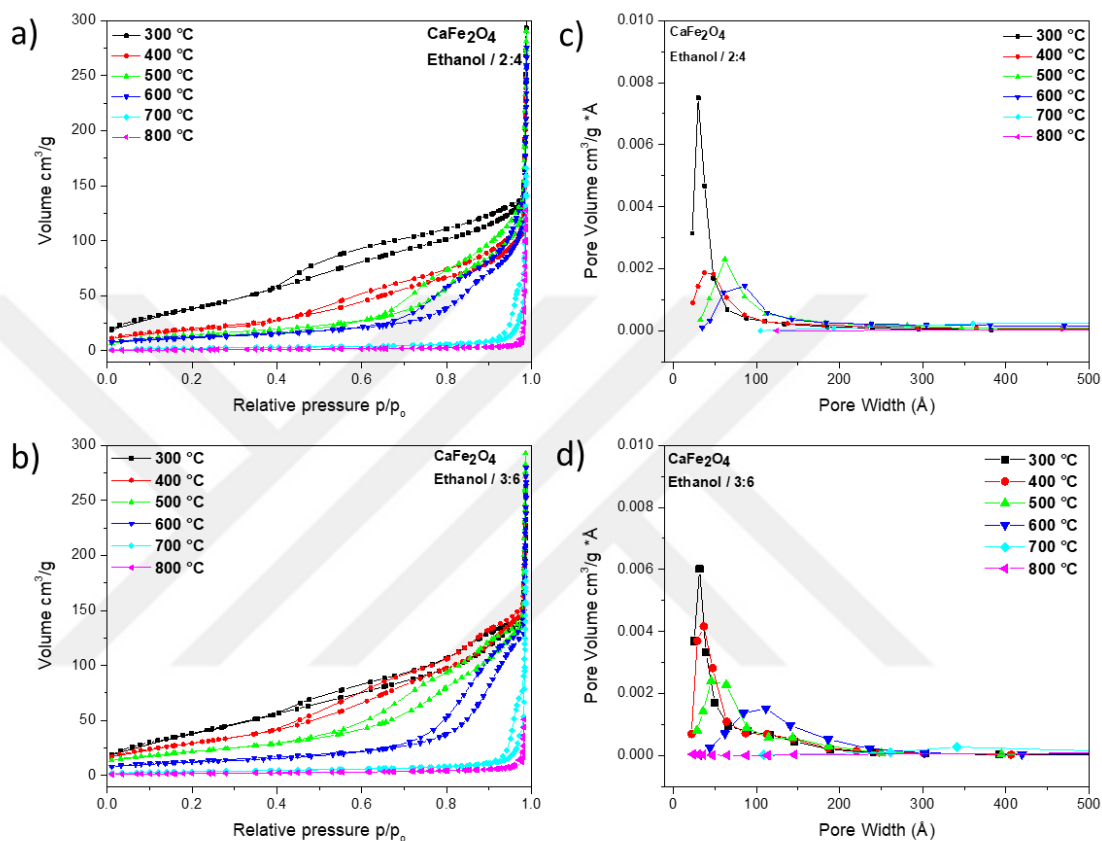


**Figure 3. 46.** (a) and (b)  $\text{N}_2$  (77K) adsorption-desorption isotherms for 2:4 and 3:6 mole ratio, (c) and (d) pore size distribution plots for same ratios.

| Calcination Temperature (°C) | Surface Area (m <sup>2</sup> /g) | Surface Area (m <sup>2</sup> /g) |
|------------------------------|----------------------------------|----------------------------------|
|                              | <b>2:4</b>                       | <b>3:6</b>                       |
| <b>300 °C</b>                | <b>145</b>                       | <b>144</b>                       |
| <b>400 °C</b>                | <b>73</b>                        | <b>108</b>                       |
| <b>500 °C</b>                | <b>54</b>                        | <b>78</b>                        |
| <b>600 °C</b>                | <b>43</b>                        | <b>46</b>                        |
| <b>700 °C</b>                | <b>9</b>                         | <b>12</b>                        |
| <b>800 °C</b>                | <b>4</b>                         | <b>7</b>                         |

**Table 3. 5.** Surface areas of CFO powders prepared by using ethanol as a solvent at various calcination temperatures

The morphological characteristics of calcined CFO particles at various temperatures were studied using SEM imaging, as illustrated in Figures 3.47 (for a 2:4 mole ratio) and 3.48 (for a 3:6 mole ratio). The images revealed that, at lower temperatures, a thin film-like morphology was observed for each mole ratio and persisted up to 600 °C, with consistent morphology observed across all films. Notably, at higher temperatures (700 and 800 °C), a thin film morphology was retained but accompanied by expanded pores. This is evident in Figure 3.47. (c) and (d), where the morphology is maintained as a thin film with expanded pores visible even at 800 °C. The presence of tiny pores in the thin films obtained by calcination at 300 °C is visible in the TEM image shown in Figure 3.47 (e), while the crystallinity of CFO calcined at 700 °C is demonstrated in Figure 3.47 (f) by the presence of visible lattice fringes.

The morphological characteristics of CFO powders with a 3:6 mole ratio calcined at different temperatures were also examined using SEM imaging, as shown in Figure 3.48. This mole ratio sample exhibited a consistently smooth and flat thin film morphology, with pore sizes too small to be visible by SEM at lower calcination temperatures. Remarkably, even at the highest calcination temperature of 800 °C, the thin film morphology was still retained in this sample, accompanied by the appearance of expanded pores with a micro- or nanochannel-like appearance, as revealed by SEM imaging in Figure 3.48 (e) and (g). This suggests that CFO powders in the 3:6 mole ratio exhibit a one-phase formation even at high calcination temperatures.

Such morphology is highly desirable in electrochemical experiments for addressing energy problems, as the expanded pores increase the likelihood of penetration by charge carriers and electrolytes, allowing more material to be accessed via the pores and thereby increasing current density. These findings provide valuable insights into the morphological characteristics of CFO particles and their potential application in electrochemical systems.

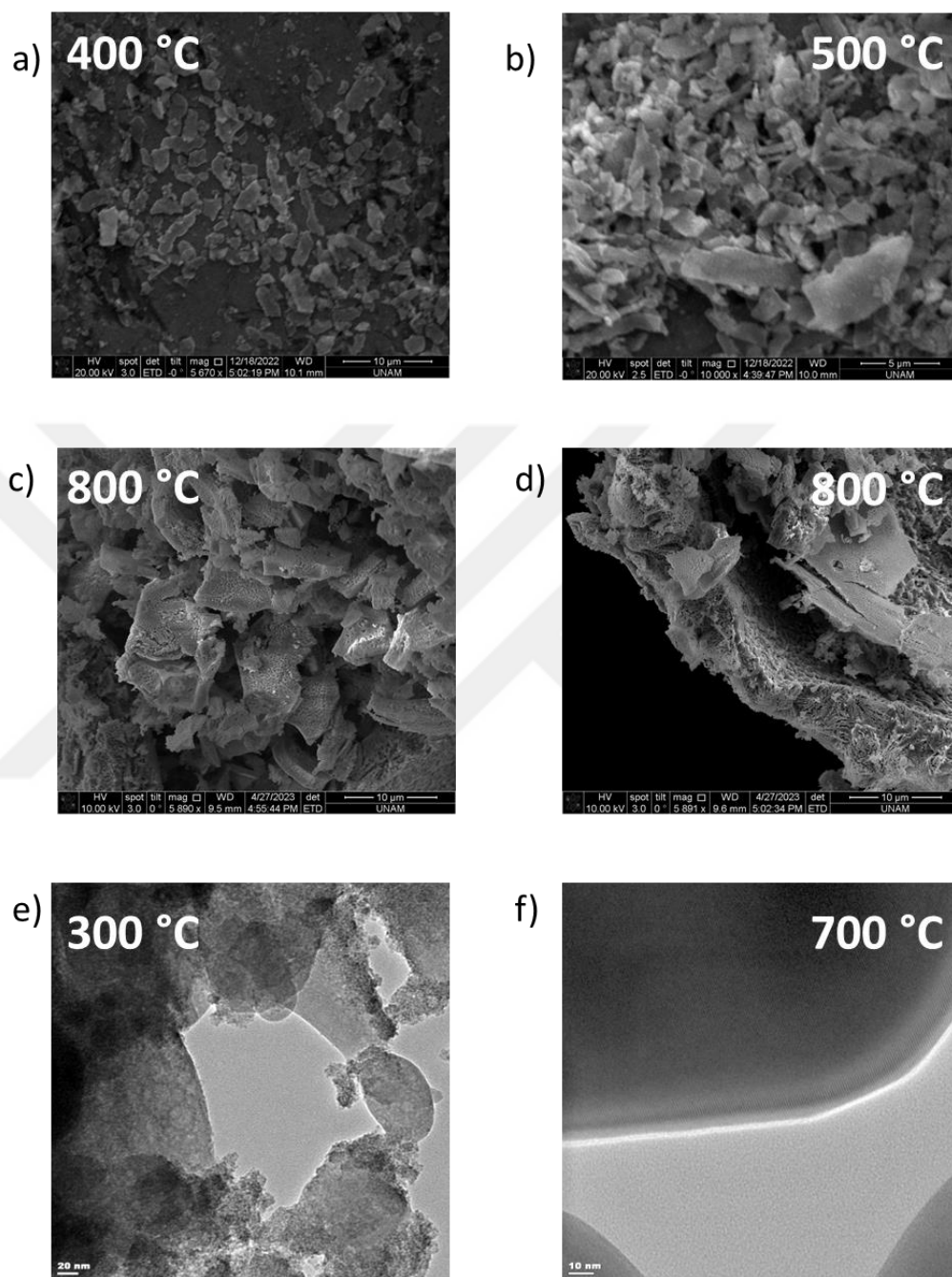


**Figure 3. 47.** SEM images of m-CFO-Eth-2:4-XXX samples prepared at various temperatures, including (a) at 400 °C and (b) at 500 °C with scale bars of 10 μm and 5 μm, respectively; (c) at 800 °C with a scale bar of 10 μm; (d) at 500 °C with a scale bar of 10 μm; (e) and (f) TEM Images at 300 °C and 700 °C with scale bars of 20 nm and 10 nm, respectively.

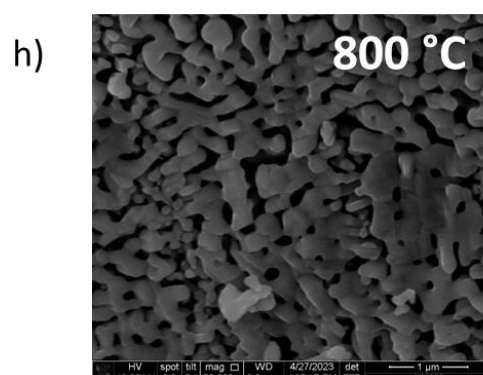
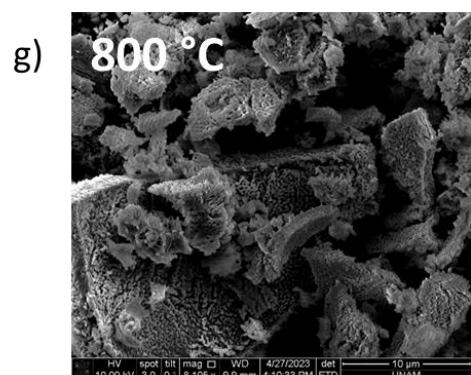
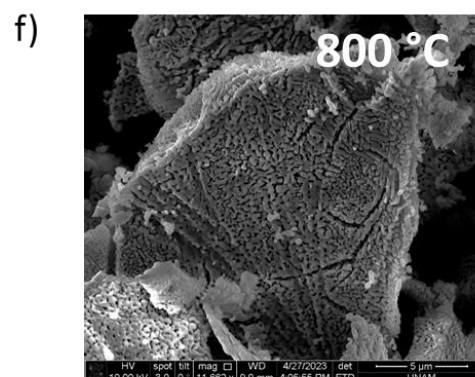
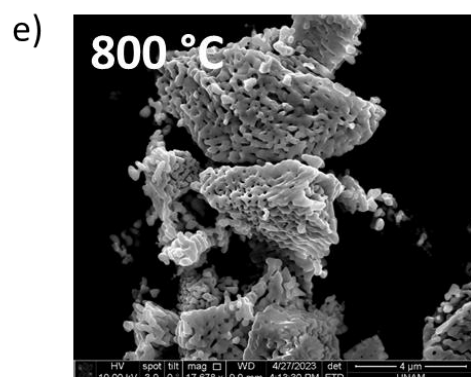
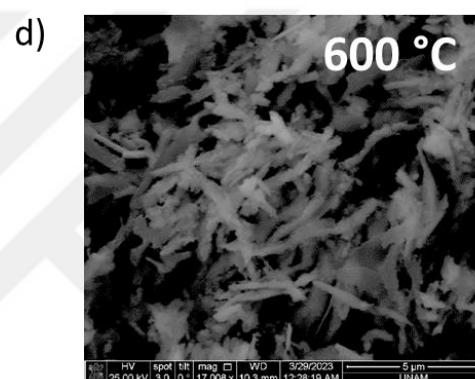
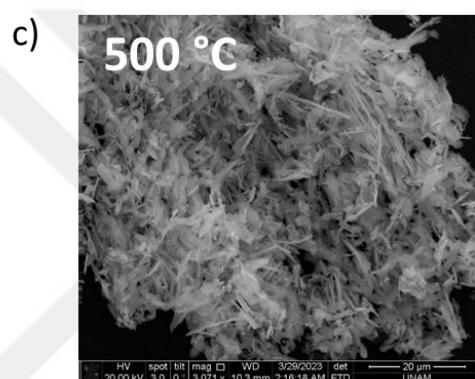
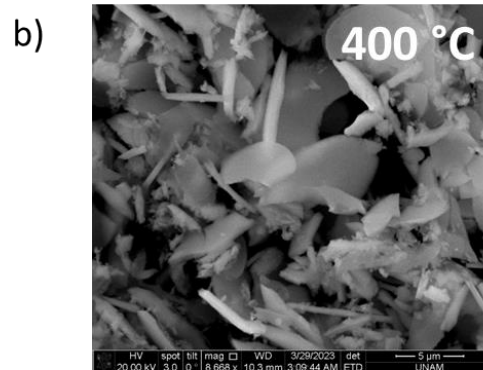
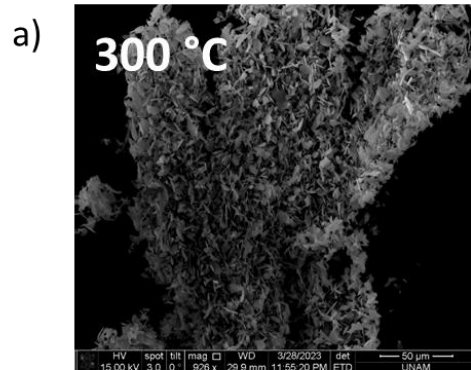


**Figure 3. 48.** SEM images of m-CFO-Eth-3:6-XXX samples prepared at various temperatures, including (a) at 300 °C and (b) at 400 °C with scale bars of 50  $\mu\text{m}$  and 5  $\mu\text{m}$ , respectively; (c) at 500 °C with a scale bar of 20  $\mu\text{m}$ ; (d) at 600 °C with a scale bar of 5  $\mu\text{m}$ ; (e) - (h) at 800 °C with scale bars of 4  $\mu\text{m}$ , 5  $\mu\text{m}$ , 10  $\mu\text{m}$ , and 1  $\mu\text{m}$ , respectively.

### 3.1.7. Mesoporous $\text{CaFe}_2\text{O}_4$ Thin Films as Electrocatalyst for Oxygen Evolution Reaction (OER)

Similarly, the solutions were coated over graphite rods by dip-coating method and calcined to prepare the electrodes at each calcination temperature (decoded as G-CFO-Eth-Ca:Fe-XXX, where G stands for graphite rod, CFO is  $\text{CaFe}_2\text{O}_4$ , Eth represents ethanol as a solvent, Ca : Fe is the calcium to iron mole ratio, and XXX is the calcination temperature in Celcius). The electrochemical experiments were also performed to analyze the electrochemical performance of the G-CFO-Eth-2:4-XXX and G-CFO-Eth-3:6-XXX electrodes in OER.

As it is described earlier. An electrode is subjected to electrochemical measurements in each experiment to analyze its catalytic activity. The electrodes prepared by using ethanol as solvent were treated differently than described in the case of water. Here, a single electrode was used in all electrochemical measurements as follows:

- 3 CVs for fresh electrodes,
- multistep chronoamperometry (CA) for Tafel slope analysis (0.3-0.7 V),
- then another 3 CVs,
- chronopotentiometry (CP) at 1mA for 2 hours,
- 3 more CVs,
- chronopotentiometry (CP) at 10 mA for 2 hours
- 3 more CVs,
- chronopotentiometry (CP) at 100 mA for 2 hours
- 3 more CVs,
- Multistep-chronopotentiometry (m-CP) for 2.5 hours, and 3 more CVs
- 100 more CVs.

Figure 3.49. shows cyclic voltammograms for each temperature of the electrodes, prepared using two different mole ratios. The left side graphs' is for the 3:6 mole ratio, and the right is for the 2:4 mole ratio. Firstly, for the 3:6 mole ratio, current densities are higher than the electrodes prepared by the 2:4 mole ratio. However, it is apparent that the current densities are decreasing for the electrodes prepared by using a 3:6 mole ratio-, which may indicate that these electrodes are unstable at lower temperatures, such as 300 °C and 400 °C. The current densities of the electrodes that were annealed at 500 and 600 °C are substantially more stable, and this is true even after nearly 14 to 15 hours of continuous use. The current densities decrease as calcination temperatures increase, which may result from reduced surface area.

Secondly, in the case of the 2:4 mole ratio, we observed that the current densities are getting higher with prolonged usage, which can be because of decreased resistance or better conductivity with use. Also, it is noticeable that in the case of a lower mole ratio, the current density increases with the temperature increase. A possible explanation for this phenomenon can be the expanded pores at higher temperatures which are more accessible. That's why the current density is the same or getting enhanced.

For each mole ratio and temperature, every single electrode was also subjected to 100 cycles of cyclic voltammetry after the end of each electrochemical experiment. We observed the same effect in the case of a 3:6 mole ratio; the current density is slightly lower at lower and stable at higher temperatures, possibly because of better crystallinity. But in the case of a 2:4 mole ratio, the current density for each temperature increases every time by usage, correlating the above discussion.

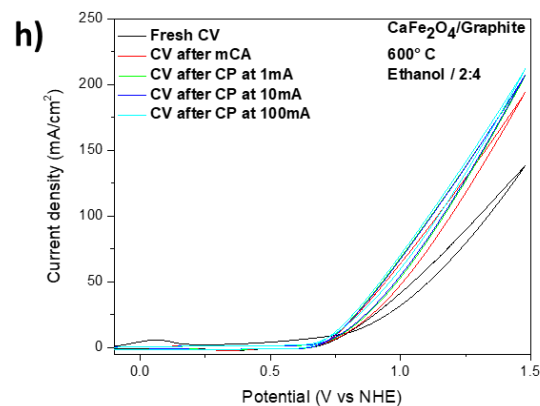
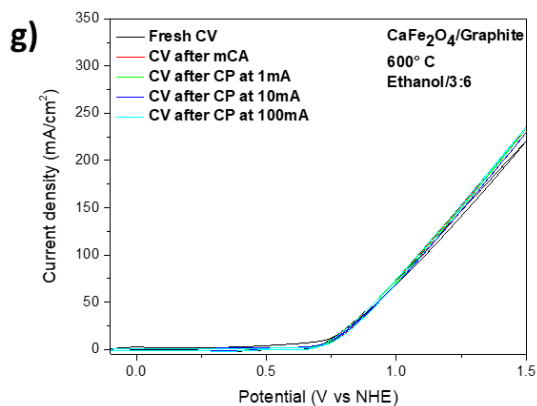
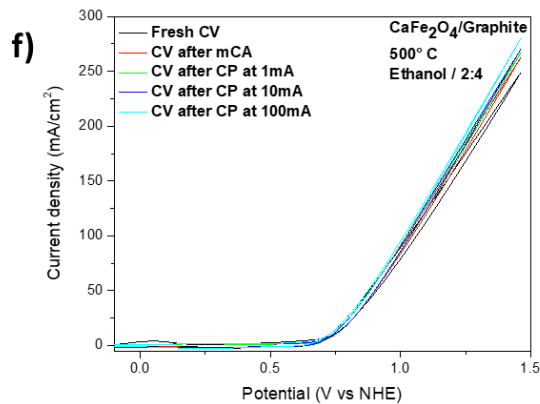
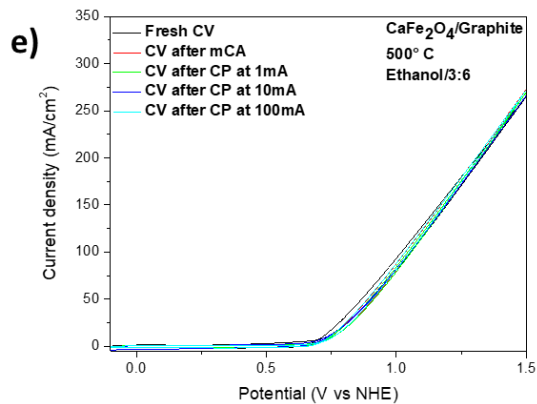
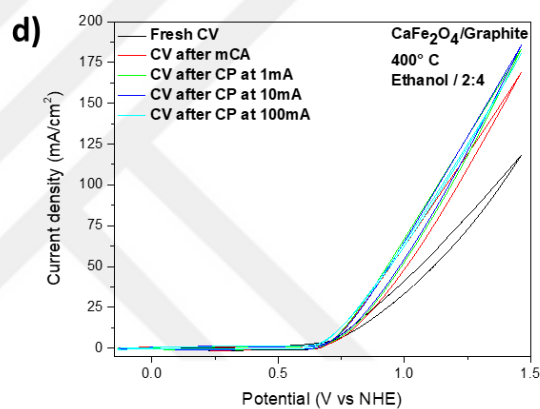
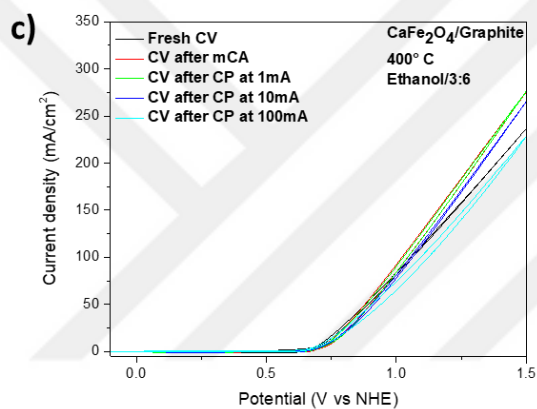
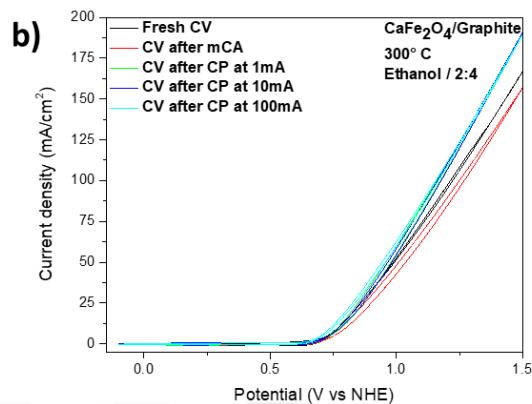
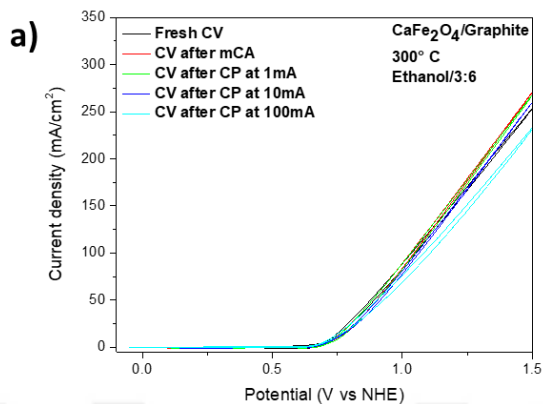


**Figure 3. 49.** Comparison of CVs after each experiment for the analysis of performance of electrodes, left column for G-CFO-Eth-3:6-XXX calcined at **(a)** 300 °C **(c)** 400 °C **(e)** 500 °C, and **(g)** 600 °C, and right column for G-CFO-Eth-2:4-XXX calcined at **(b)** 300 °C **(d)** 400 °C **(f)** 500 °C, and **(h)** 600 °C.



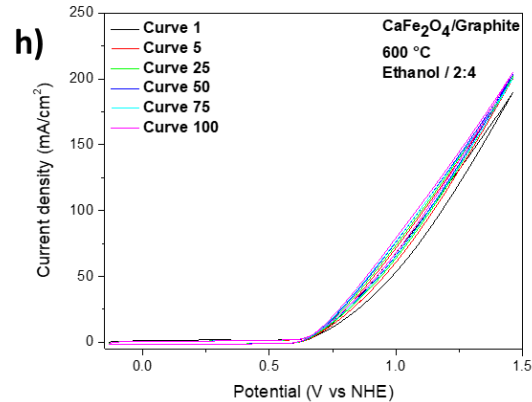
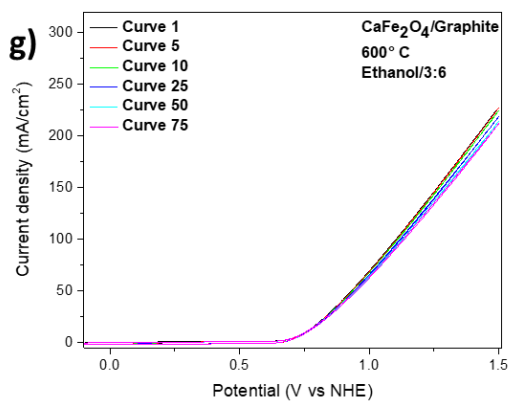
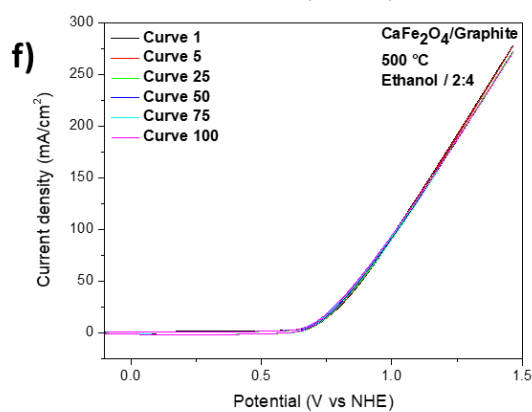
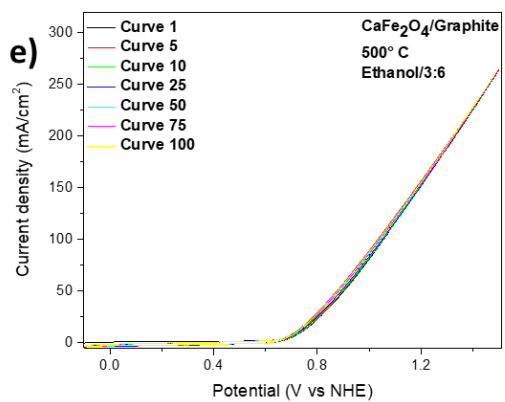
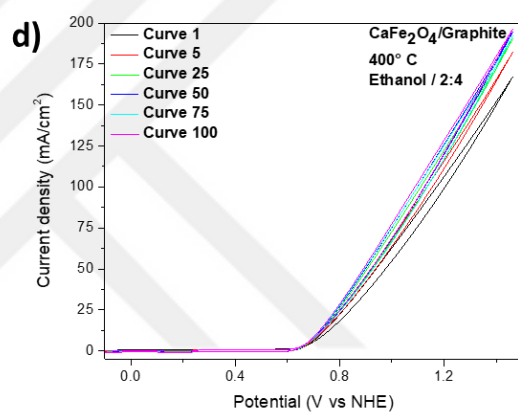
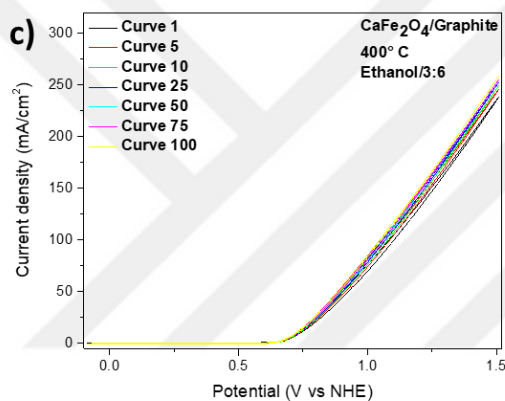
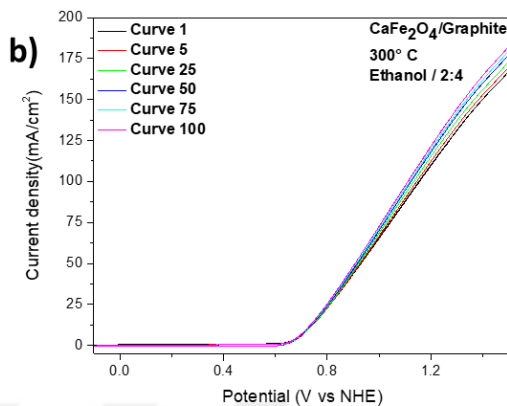
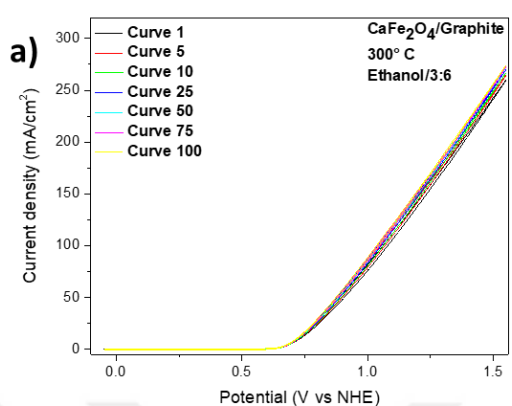


**Figure 3. 50.** Multiple CVs to analyze the stability of electrodes, a left column for G-CFO-Eth-3:6-XXX calcined at **(a)** 300 °C **(c)** 400 °C **(e)** 500 °C, and **(g)** 600 °C, and a right column for G-CFO-Eth-2:4-XXX calcined at **(b)** 300 °C **(d)** 400 °C **(f)** 500 °C, and **(h)** 600 °C.

Similarly, as we did for the water case, the overpotentials are determined from 2 h CP experiments for each electrode, calcined at different temperatures, at different current densities, namely 1, 10, and 100 mA/cm<sup>2</sup>. We observed different trends for two different mole ratios. For the 2:4 mole ratios, we observed that the overpotentials for each current density decrease with increasing annealing temperature. For instance, from Figure 3.51, it is shown that the difference in the overpotentials for different electrodes calcined at different temperatures is minimal. We observed that for an unknown reason, the electrode calcined at 400 °C showed instability under harsh conditions, i.e., at 100 mA. Still, the rest are stable in extreme conditions, even for more prolonged usage.

For the 3:6 mole ratio, there is no specific trend between the overpotentials and annealing temperature. But the overpotentials are approximately the same as for the 2:4 mole ratio. Also, in this case, the electrodes are not as stable for the lower temperatures, and they showed an increase in overpotential under harsh conditions, which is precisely relatable to cyclic voltammograms as we showed earlier that for the 3:6 mole ratio, the current density is decreased with usage for a longer time. Most importantly, the overpotentials are very low. For example, for the 3:6 mole ratio and 300 °C calcined electrode, the overpotential at 1 mA/cm<sup>2</sup> is 258 mV, and at 10 mA/cm<sup>2</sup> is 356 mV. It is just more than one tafel slope value and less than two Tafels, which indicates excellent catalytic activity and stability of electrodes.

The multistep chronopotentiometry (mCP) measurements were also done to determine the overpotentials at other current densities using each electrode, prepared by different mole ratios and calcined at different temperatures. The m-CP is carried out in ten steps, ranging the current densities from 10 to 100 mA/cm<sup>2</sup>, and the potential values are recorded for 15 min at each step, see Figure 3.52. As shown in Figure 5.13, each step is flat enough,

indicating each electrode's stability at each current density. Again, in the case of a 2:4 mole ratio, it is clear that overpotentials are getting reduced with an increase in temperature, and in the case of a 3:6 mole ratio, there is a reverse case.

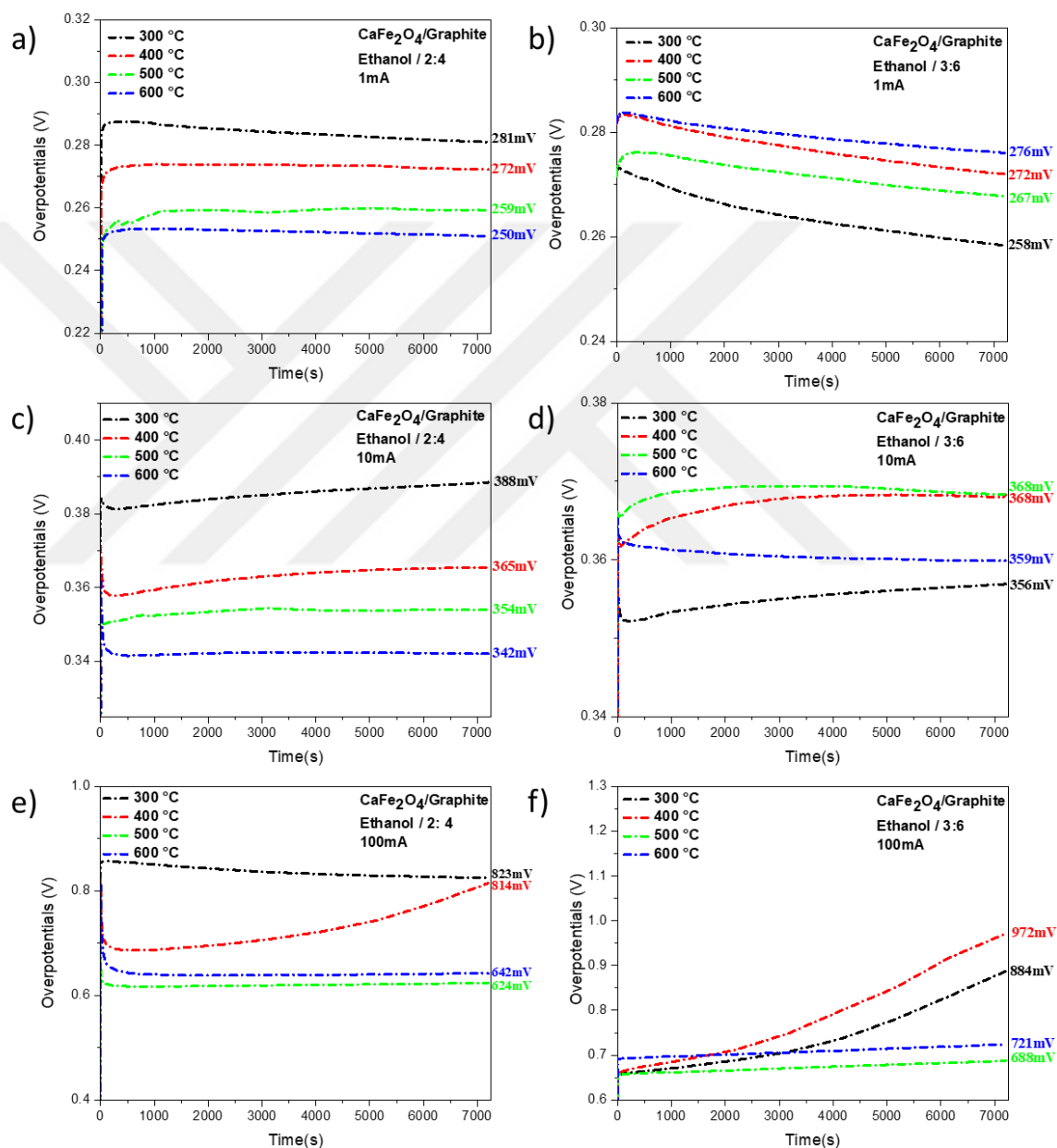


**Figure 3. 51.** Chronopotentiometry (CP) plots showing the overpotentials versus time for all electrodes, with the left column representing G-CFO-Eth-2:4-XXX and the right column representing G-CFO-Eth-3:6-XXX at various temperatures. Each plot shows the

overpotential at different current densities, including (a) and (b) at  $1 \text{ mA cm}^{-2}$ , (c) and (d) at  $10 \text{ mA cm}^{-2}$ , and (e) and (f) at  $100 \text{ mA cm}^{-2}$ , for 2 hours.

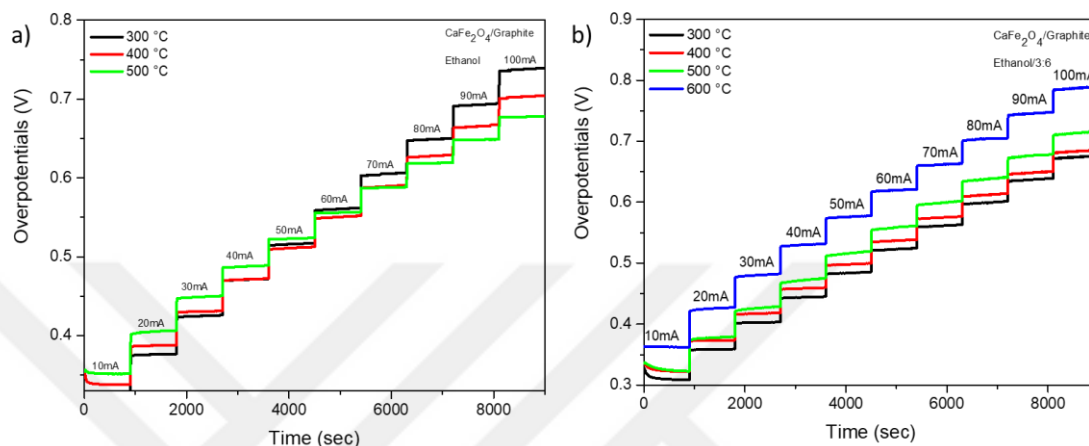


**Figure 3. 52.** Multistep-Chronopotentiometry (m-CP) plots showing the overpotentials versus time for all electrodes at various current densities, (a) G-CFO-Eth-2:4-XXX and (b)G-CFO-Eth-3:6-XXX at various temperatures. Each step took 15 minutes.

Again, multistep chronoamperometry experiments are conducted to determine the Tafel slopes of each electrode. Tafel slope is related to the kinetic of OER, involving rate and mechanism. For the 2:4 mole ratio, the Tafel slopes are very similar for all electrodes, calcined at different temperatures, and may indicate that the water oxidation reaction occurs through the same mechanism. But for the 3:6 mole ratio, the Tafel slope gradually increases with increasing annealing temperature, implying that the catalytic sites on the electrode surface change with heating at higher temperatures. This can be the possible reason for the rise in the Tafel slope with increasing annealing temperature. Figure 3.53 shows the tafel slope values for each temperature and mole ratio.

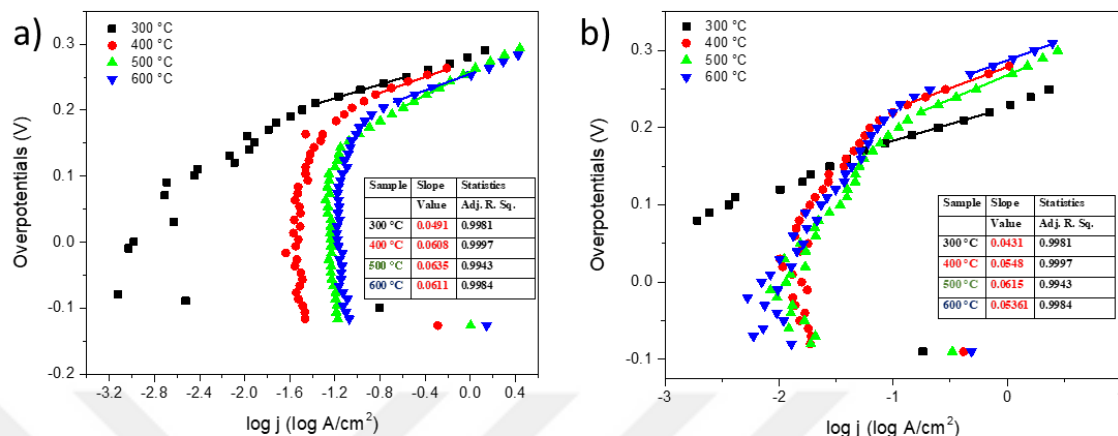


**Figure 3. 53.** Temperature dependent Tafel slopes of the (a) G-CFO-Eth-2:4-XXX and (b) G-CFO-Eth-3:6-XXX electrodes.

### 3.1.8. Effect of thickness on catalytic activities of CFO-coated electrodes

This experiment aimed to investigate the effect of the thickness of a coated material on a graphite substrate on its catalytic activity. This is achieved by varying the thickness of the coating material by using diluted solutions; four solutions are prepared by diluting the mother liquor 10, 20, 50, and 100 times. After that, we fabricated the electrodes with these compositions by dip coating at calcined at 600 °C.

After preparation, we performed three cycles of cyclic voltammetry on each electrode of each dilution to establish a baseline for comparison. We subsequently subjected each electrode to water oxidation under harsh conditions (100 mA/cm<sup>2</sup> for 2 h) to simulate the impact of prolonged usage on the electrode. Following this, we conducted another set of three cycles of cyclic voltammetry to compare the efficiency of the electrodes before and after exposure to harsh conditions. The cyclic voltammetry measurements provided valuable insight into the efficiency of the electrodes before and after the water oxidation test, allowing us to conclude the effect of coating thickness on electrode performance under harsh conditions.

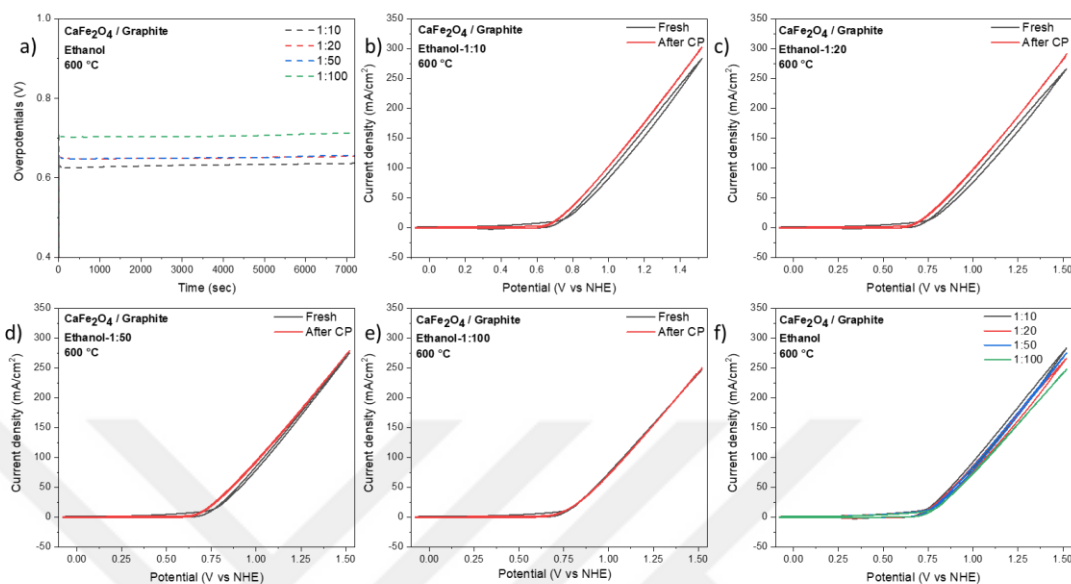


**Figure 3. 54.** (a) CP plots showing the overpotentials versus time for all electrodes prepared using different dilutions, with (b) to (e) representing before and after CV for each electrode with different dilutions, including (b) 1:10, (c) 1:20, (d) 1:50, and (e) 1:100. Additionally, (f) shows the comparison of all CVs.

Figure 3.54. shows that the overpotential of the electrode, prepared from the 100 times diluted solution is similar to that of the 10 times diluted electrodes, indicating excellent stability for even very thin film electrodes. The slight variation in the overpotential between the electrodes of different thicknesses is negligible and can also be observed for electrodes of similar thickness and composition. Multiple factors contribute to electrode activity, such as the last drop of the solution on the bottom in dip coating, time differences in the polymerization of iron species during electrode preparation, human errors in maintaining a consistent electrode area (which cannot be precisely 1 cm<sup>2</sup> at all times), and other factors.

To evaluate the efficiency of the electrodes, we compared cyclic voltammograms before and after usage. We observed an improvement in current density for each electrode after use, and the cyclic voltammograms shifted towards more negative potentials, indicating a decrease in resistance and improved conductivity of the electrodes. Figure 5.15

demonstrates that the current densities for each electrode with different compositions are nearly identical.

Figure 3.55. shows x-ray photoelectron spectroscopy (XPS) results, demonstrating that decreasing the thickness of the working electrodes decreases the intensity of the Fe-2p, Ca-2p, and O-1s peaks. The C-1s region is less regular, but it indicates that a reduction in sample thickness of the working electrode reveals more graphite, resulting in a higher C-1s peak intensity with decreasing film thickness.

All XPS spectra were recorded before electrochemical experiments using the same electrodes. However, attempts to analyze the same electrodes after electrochemical experiments were unsuccessful due to a significant accumulation of KOH and  $\text{KHCO}_3$  crystals, resulting in undetectable intensities from the calcium and iron species. Despite attempts to remove the KOH by dissolution in water and washing with dilute acid, XPS results showed a substantial amount of potassium on top of the electrodes. Potassium ion intercalation into graphite electrodes is a possible explanation for this phenomenon, and thus it isn't easy to eliminate potassium ions entirely.

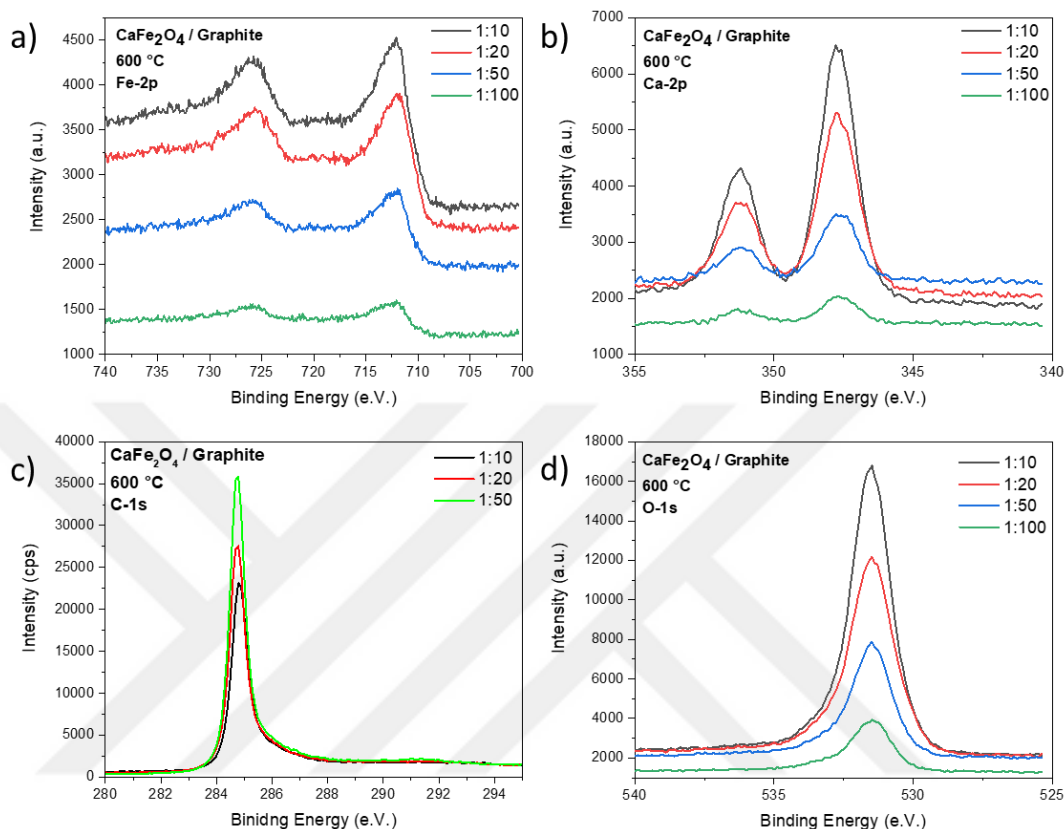


**Figure 3. 55.** X-ray photoelectron spectroscopy (XPS) spectra of G-CFO-Eth-2:4-XXX, obtained at different dilutions and calcination at 600 °C: High-resolution spectra in the (a) Fe-2p, (b) Ca-2p, (c) C-1s, and (d) O-1s regions.

In an attempt to further explore the potential of highly diluted working electrodes, we conducted experiments with dilutions up to 1:500 and annealed them at 600°C. However, we found that the results were not reproducible due to insufficient sample on the graphite electrode, leading to instability under harsh conditions. Despite this, XPS analysis indicated that the sample still coated the graphite surface, albeit at deficient amounts. Ca 2p and O 1s peaks intensity are plotted with respect to the number of dilutions to find the relationship between the dilution and film thickness; see Figure 3.56. Ca 2p peak fits very well (with an  $R^2$  of 0.99998) to an exponential function as expected. However, the fit is not as good in the O 1s peak intensity, likely due to unpredictable deposition of

bicarbonate species. Therefore, Ca 2p region can be used to compare the film thickness or surface coverage on the graphite surface. According to the plot in Figure 3.55, the surface coverage drops by 1.43 times by diluting 10 to 20 times (2 times) and almost nine times by diluting 100 times. This could be directly related to drop in film thickness or surface coverage and valuable to evaluate the efficiency of the electrodes in OER.

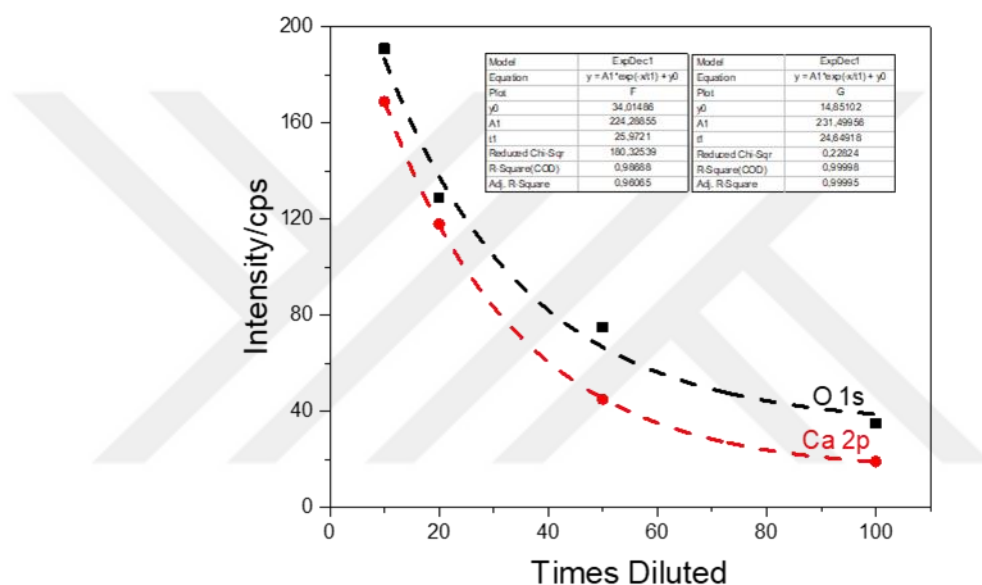


**Figure 3. 56.** Plot of Ca-2p and O-1s between Intensities vs. dilution

Additionally, we tested the idea using electrodes, calcined at lower temperatures, specifically 300 °C, but found that the potential is not constant at lower temperatures for highly diluted samples, even at 50 times dilution. We concluded that the thickness of the coated material is not critical for water oxidation as charge carriers cannot penetrate the pores of the material. Therefore, the surface reaction is the primary factor in determining electrode activity, with pore shape being the critical characteristic. Furthermore, at higher temperatures, surface structures grow to open deeper, longer pores with irregularities and increase top active surface area, contributing to activity in harsh conditions despite the small amount of coated material.

We also tested highly diluted electrodes at 300 and 500 times dilution in less harsh conditions, specifically CP at 10 mA / cm<sup>2</sup> for two hours, and found that they were stable. Figure 3.57 shows CP plots for 1:300 and 1:500 diluted samples; we found that for the significantly diluted samples, results are not reproducible; for instance, it can be seen that, in Figure 3.57 (b), the overpotentials are getting increased for each sample, but in figure 3.57 (c) it can be seen in CP plots that overpotentials are quite constant and not getting increased with the usage of electrodes indicating the excellent stability of electrodes even for such electrodes prepared by highly diluted solutions. This suggests that highly diluted electrodes annealed at higher temperatures (600°C) are suitable for use in ambient conditions. Finally, our results indicate that these types of energy materials (CFO) performance depends on the surface's characteristics rather than the coating material's thickness or the pores' size. Also, we found it unnecessary to waste a large amount of metal salts to fabricate these materials, as performance will be similar regardless of coating thickness.

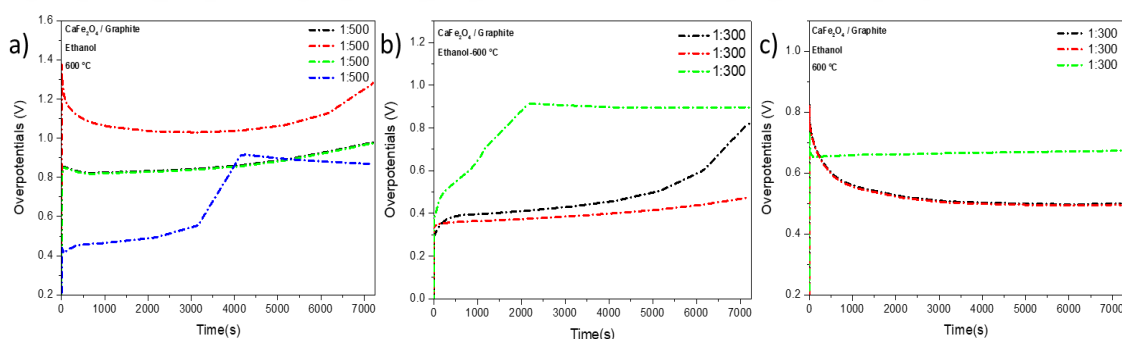


**Figure 3. 57.** CP plots of overpotential versus time for the electrodes, prepared using different dilutions, (a) 1:500 dilution, (b) and (c) 1:300 dilution.

To further characterize, we also used UV-Vis spectroscopy and XRD as valuable techniques. The solutions up to 100 times dilution were off-scaled in the spectra, therefore, their spectra were recorded by coating the solutions (without dilution, 1:5, 1:10, and 1:20) on glass slides to overcome this problem. It can be seen that in Figure 3.58 (a), the absorption peak for the undiluted sample is visible. Still, the other dilutions mentioned above follow the concentration trend. However, their intensities are quite low (just above

the reference baseline), possibly because of the thin film coated on a glass slide with low sample concentration. But the 1:200, 1:300, and 1:400 diluted solutions were directly measured in the solution phase (Figure 3.58 (b)). However, the undiluted coated samples display a peak at around 420 nm that is blue-shifted to below 350 nm in the ethanol solutions.

Similarly, we coated all solutions of varying dilutions on microscopic glass slides and recorded their small-angle XRD patterns for fresh and 1-day-aged samples to analyze the formation of mesophases. We noticed that even with 300 dilutions, we could observe weak and broad diffraction, confirming the formation of mesophases. Fig 3.58 (c) indicates the XRD patterns for the same glass slides aged for one day. Again, the line around  $3^\circ$  indicates the leaching out of surfactants, as we observed without dilution.

Similarly, we coated all solutions of varying dilutions on microscopic glass slides and recorded their small angle XRD patterns for fresh and 1-day-aged samples to analyze the formation of mesophases. We noticed that even with 300 dilutions, we could observe very less and broad diffraction, confirming the formation of mesophases. Fig 3.58 (d) indicates the XRD patterns for the same glass slides aged for one day. Again, the line

around 3° indicates the leaching out of surfactants, as we observed in the case of without dilution.

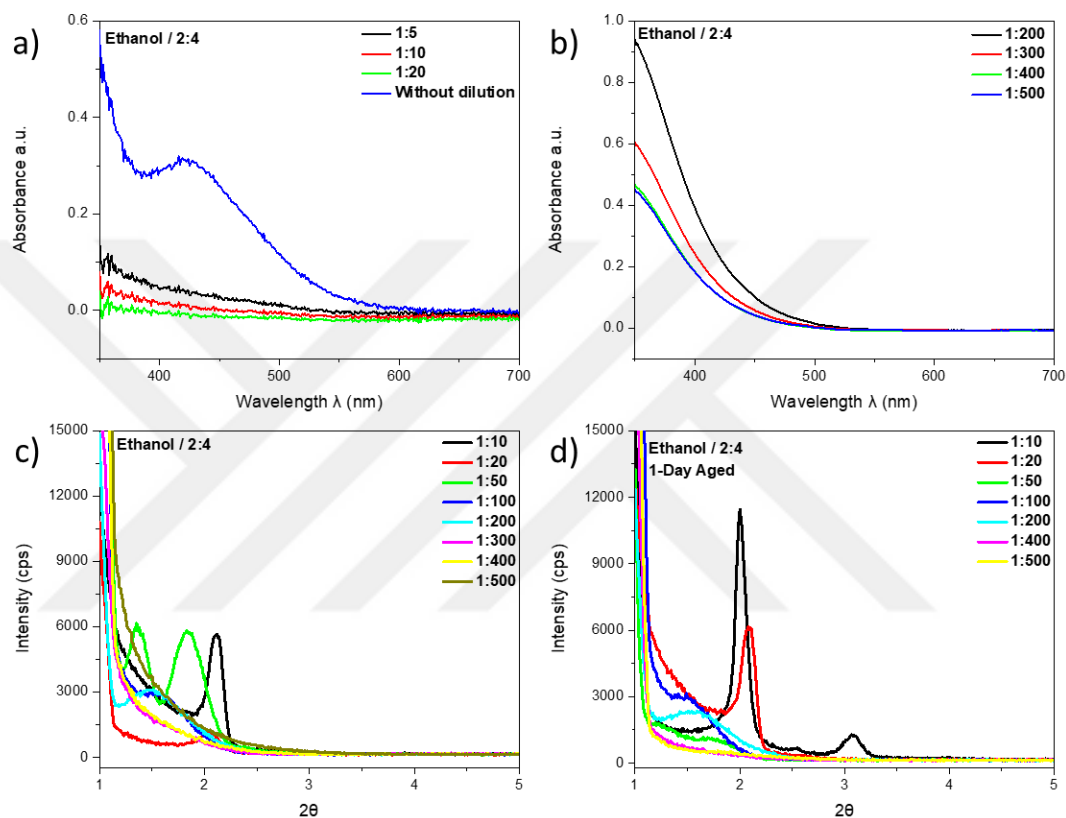


**Figure 3. 58.** Visible spectra and XRD patterns for solutions of different dilutions. (a) Visible spectra of fresh solutions coated on glass slides. (b) Visible spectra of fresh solutions in the quartz sample holder. (c) Small angle XRD patterns of fresh solutions with different dilutions coated on glass slides. (d) XRD pattern for same glass slides aged for 1 day.

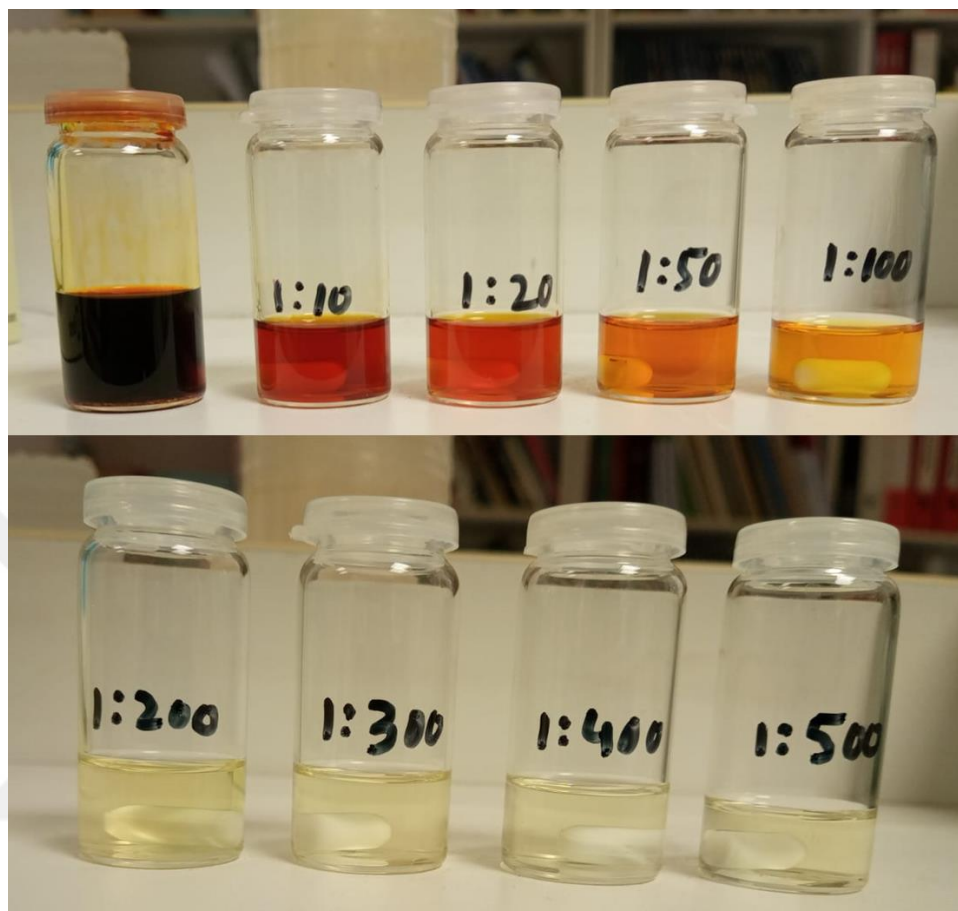


**Figure 3. 59.** Image of colored solutions of different dilutions used for the fabrication of electrodes

## Chapter 4

### 4.1. Synthesis and Characterization of Mesoporous Fe<sub>2</sub>O<sub>3</sub> thin films:

We also prepared the mesoporous iron oxide material to compare it with the CaFe<sub>2</sub>O<sub>4</sub> in terms of morphology, mesophase formation, and catalytic activity. The composition of ingredients used in the synthesis is given in Table 6.1.

| Fe<br>(NO <sub>3</sub> ) <sub>2</sub> .9H <sub>2</sub> O<br>(g) | CTAB<br>(g) | C <sub>12</sub> EO <sub>10</sub><br>(g) | Water<br>(g) |
|-----------------------------------------------------------------|-------------|-----------------------------------------|--------------|
| 1.27g                                                           | 0.287       | 0.5                                     | 5            |

**Table 4. 1.** Amounts of chemicals used in Fe (NO<sub>3</sub>)<sub>2</sub>.9H<sub>2</sub>O- C<sub>12</sub>EO<sub>10</sub>-CTAB-Ethanol solution.

The small-angle XRD pattern shows a broad diffraction at around 1.9°, 2θ, indicating that a mesophase is not well-ordered. It is apparent from the figure that after 60 minutes, the

intensity of broad diffraction enhances. Comparing it with  $\text{CaFe}_2\text{O}_4$  reveals that calcium plays a crucial role in forming ordered mesophases.

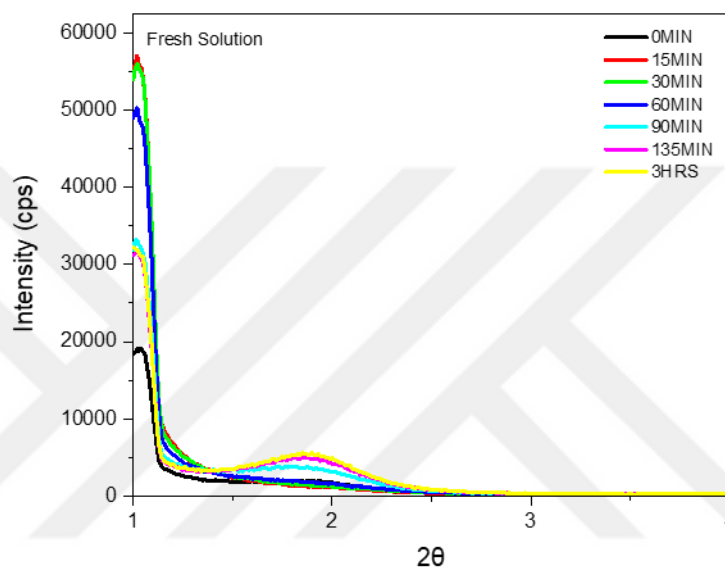


**Figure 4. 1.** Small-angle XRD patterns for LLCs prepared from a fresh solution of Iron only.

The coated LLC sample is calcined by annealing up to 400 °C and analyzed using ATR-FTIR and XRD techniques. The IR studies (Figure 6.2) show that iron oxide (hematite  $\text{Fe}_2\text{O}_3$ ) is formed at 400 °C. The peak at significantly lower wavelengths at  $514\text{ cm}^{-1}$  and  $427\text{ cm}^{-1}$  confirms the formation of iron oxide, according to the literature [98]. The wide angle XRD pattern shows the crystalline iron oxide formation at 400 °C, and it can be indexed using pdf card number 00-033-0664.

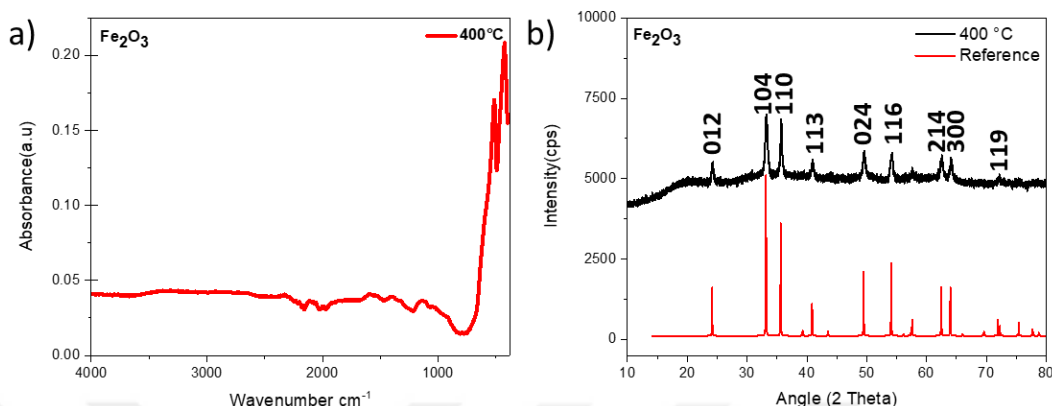


**Figure 4. 2.** Iron oxide sample, calcined at 400 °C: (a) ATR-FTIR spectrum and (b) XRD pattern with the reference pattern.

Graphite is dip-coated using the same solution, calcined at 300 °C (denoted as G- $\text{Fe}_2\text{O}_3$ ), and used for electrochemical measurements. The catalytic activity of OER reveals that there are more overpotentials at higher current densities compared to  $\text{CaFe}_2\text{O}_4$  (Figure 4.3). The good thing is that, again, with the usage of the electrode, its performance improved (Figure 4.3(c)). The multi-step chronopotentiometry shows the overpotentials at different current densities, which are a bit higher than  $\text{CaFe}_2\text{O}_4$  (specially prepared by chloride precursors).

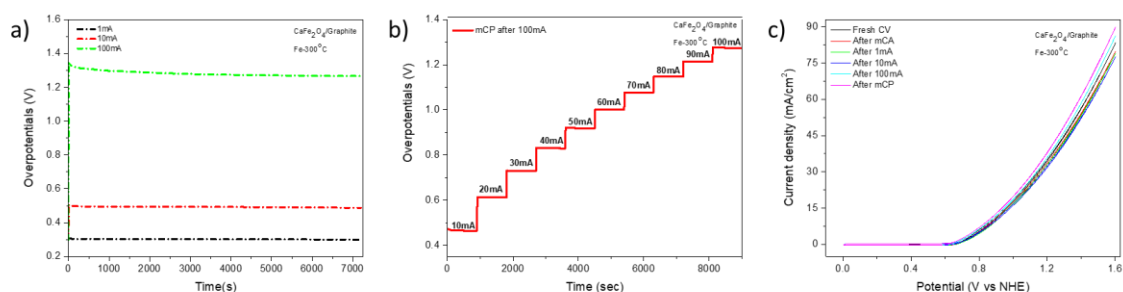


**Figure 4. 3.** (a) CP plots showing overpotential versus time for the electrodes, prepared only with iron at 1, 10, and 100  $\text{mA}/\text{cm}^2$  current densities. (b) m-CP plot at different current densities to analyze the electrode's performance with usage. (c) Comparison of CVs after each experiment to evaluate the electrode's stability and activity.

The scan-rate-dependent measurements are also done for the working electrodes, prepared using only iron precursor. The same experiments using the same technique and parameters are carried out as described earlier. Figure 6.4 displays scan rate-dependent CVs using fresh and used electrodes and  $\log(I)$  versus  $\log(v)$  ( $v$  is scan rate in mV/s) plots. The slope of linear fit (almost 1.0) in these plots reveals that the process is surface-controlled. This may explain the reason for more overpotentials because the surface is only accessible to the charge carriers. However, in the case of  $\text{CaFe}_2\text{O}_4$ , the slope of a similar plot is around 0.75, which indicates that both surface and diffusion control reactions occur, and it may decrease the over-potentials and better conductivity of electrodes. To conclude, it can be said that the overpotentials while using only iron precursors (slope 1.0, i.e., surface controlled, charge carriers having no access to the pores) are more as compared to when using both calcium and iron precursors (slope 0.75, i.e., both diffusion and surface controlled) for the fabrication of electrodes.

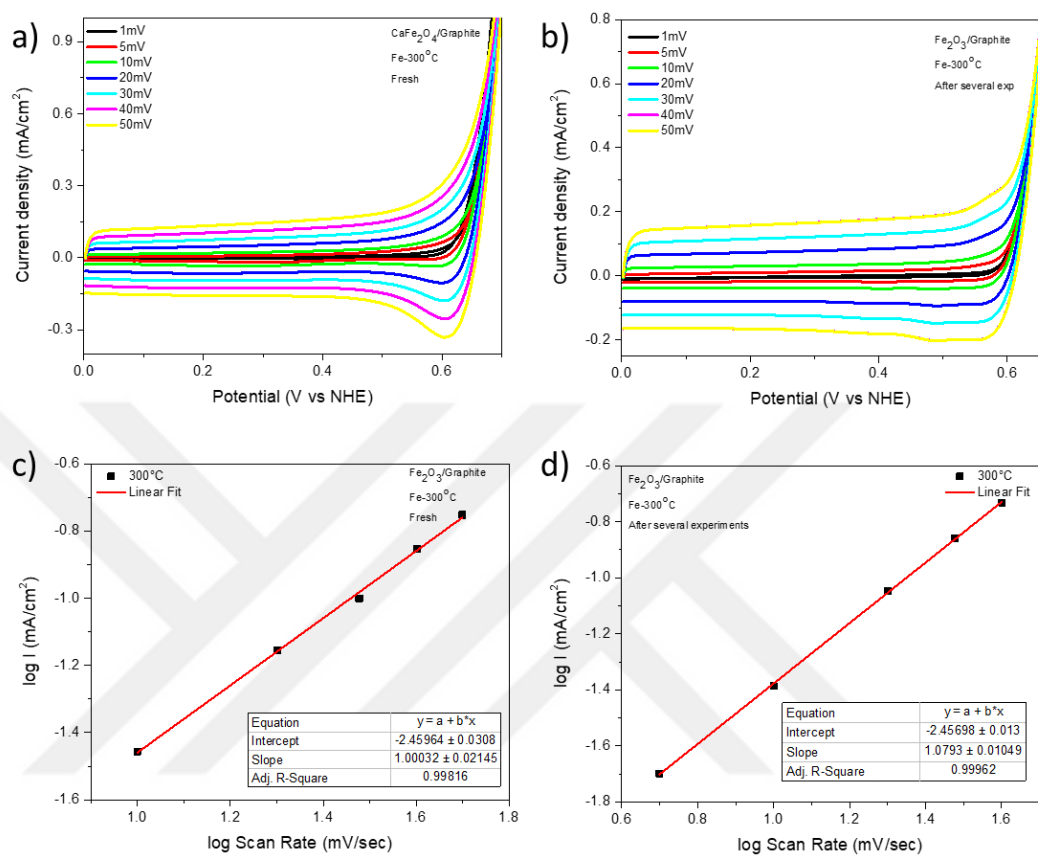


**Figure 4.** Scan rate-dependent CVs of the G-Fe<sub>2</sub>O<sub>3</sub> electrodes, calcined at 300 °C: (a) fresh, and (b) after several experiments. (c and d) Plot of log current density (log I mA cm<sup>-2</sup>) versus log scan rate (log v) plots for the G-Fe<sub>2</sub>O<sub>3</sub> fresh and used electrodes.

# Chapter 5

## 5.1. Summary

| Sample                | Overpotential<br>at 1mA cm <sup>-2</sup> | Overpotential<br>at 10mA cm <sup>-2</sup> | Overpotential<br>at 100mA cm <sup>-2</sup> | Tafel slope<br>mV/dec |
|-----------------------|------------------------------------------|-------------------------------------------|--------------------------------------------|-----------------------|
| G-CFO-300             | 280                                      | 402                                       |                                            | 56                    |
| G-CFO-400             | 260                                      | 347                                       |                                            | 59                    |
| G-CFO-500             | 270                                      | 477                                       |                                            | 83                    |
| G-CFO-600             | 277                                      | 371                                       |                                            | 62                    |
| G-CFO-Cl-300          | 270                                      | 361                                       | 732                                        | 47                    |
| G-CFO-Cl-400          | 267                                      | 358                                       | 772                                        | 54                    |
| G-CFO-Cl-500          | 250                                      | 351                                       | 760                                        | 62                    |
| G-CFO-Cl-600          | 270                                      | 391                                       | 1030                                       | 72                    |
| G-CFO-Eth-<br>2:4-300 | 281                                      | 388                                       | 823                                        | 49                    |
| G-CFO-Eth-<br>2:4-400 | 272                                      | 365                                       | 814                                        | 60                    |
| G-CFO-Eth-<br>2:4-500 | 259                                      | 354                                       | 624                                        | 63                    |
| G-CFO-Eth-<br>2:4-600 | 250                                      | 342                                       | 642                                        | 61                    |
| G-CFO-Eth-<br>3:6-300 | 258                                      | 356                                       | 884                                        | 43                    |
| G-CFO-Eth-<br>3:6-400 | 272                                      | 368                                       | 972                                        | 54                    |
| G-CFO-Eth-<br>3:6-500 | 267                                      | 368                                       | 688                                        | 61                    |
| G-CFO-Eth-<br>3:6-600 | 276                                      | 359                                       | 721                                        | 53                    |

**Table 5. 1.** General table of mesoporous calcium iron oxide synthesized using different parameters with Tafel slope and overpotential values at 1, 10, and 100 mA cm<sup>-2</sup>.

## 5.2. Conclusion:

In this thesis, we employed MASA approach to synthesize mesoporous calcium iron oxide thin films. CTAB is used as a charged surfactant to enhance the capability to stabilize the high metal salts concentrations in mesophases. We prepared the same materials using different pathways (by varying mole ratios, solvents, and precursors) to understand the mechanism of product formation and the effect of varying synthesis parameters on various characteristics (particle size, surface area, morphology, and catalytic activity).

First, water as a solvent and nitrate precursors are used to synthesize the calcium iron oxide, keeping the mole ratio of calcium to iron as 2:4. The mesophase diffracts at small angles and the diffraction lines is indexed to a body centered tetragonal phase that is anisotropic and displays characteristic POM images. Bicarbonates or surface carbonates form at low calcination temperature, and later on, they transform to calcium carbonates that are persistent up to 600 °C, and then they react with other iron species to form CFO at 800 °C in a crystalline form. The maximum surface area is 145 m<sup>2</sup>/g at 300 °C. Remarkably, the porous structure retains even at 800 °C.

Second synthesis approach involves chloride precursors and water as a solvent to synthesize the same material. This method produces crystalline iron oxide at a low temperatures with significantly less carbonates. However, the surface area is relatively low, only 5 m<sup>2</sup>/g. However, these materials show excellent stability and catalytic activities in electrochemical tests. The electrodes are stable in even harsh conditions (CP at 100 mA/cm<sup>2</sup>) and get more active with usage. Tafel slope increases from 47 mV/dec at 300 °C to 76 mV/dec, also indicating a conversion of iron oxide to CFO.

Furthermore, ethanol is employed as a solvent using nitrate precursors at two different mole ratios to prepare the same materials. Interestingly, ethanol as a solvent plays a critical role in preserving the surface areas even at higher temperatures. The surface area of the calcined sample is 146 m<sup>2</sup>/g at 300 °C and 46 m<sup>2</sup>/g at 600 °C and maintains its porous structure. The thin film morphology is retained and consistent throughout the sample with an excellent porous structure. The permeable channels are retained at such a

high calcination temperature of 800 °C, which can be extremely useful to address the energy materials, as charge carriers will have the opportunity to access the pores and utilize more material. Overpotentials are relatively low. Also, similar Tafel slope values indicate a similar mechanism for the oxygen evolution reactions.

Lastly, the thickness of coated materials on the catalytic activities in electrochemical experiments are investigated and found that the electrode thickness has no effect on the catalytic activity. OER performance of these types of energy materials is based on the characteristics of the surface being used rather than the pore size and thickness of the material. Also, the synthesis and catalytic activities of iron oxide and calcium iron oxide are compared and found out that imparting calcium plays an active role such that the efficiency of CFO is better compared to iron oxide.

## 5.3. Future Work

### 5.3.1. Influence of Solvent on the Polymerization of Iron Species; Investigating the Mechanism and Understanding the Polymerization Process

In this thesis, we have shown the effect of two solvents on synthesizing calcium iron oxide. The nitrate species are unique in monitoring iron species' hydrolysis and condensation process using IR spectroscopy. We used different solvents, methanol, ethanol, iso-propanol, t-butanol, and 2,2,2-trifluoro ethanol, to understand the polymerization mechanism of iron species in various media.

To start with 2,2,2-trifluoro ethanol (TFE), it is tough to dissolve the metal salts into this solvent. So at first, we dissolved the metal salts into methanol and then added the TFE. We prepared three different sets of solutions with varying compositions of methanol and TFE to observe the removal of nitrates. The resulting solutions were characterized by IR spectroscopy and small angle XRD measurements.

It is shown in Figure 5.1 that by increasing the amount of TFE, there is a gradual decrease in the nitrate peaks. These samples on the diamond crystal of ATR-FTIR were heated up to 100 °C, and it is prominent in figure (c) that almost all nitrates are gone even at this lower temperature. Also, mesophase formation with this solvent is possible, as shown in (d); with increasing TFE concentration, the diffraction angle shifts to lower angles with a broad mesophase line, indicating an increase in d-spacing. The SEM images for powder sample using TFE is given below showing the flake like morphology. This type of morphology may play an essential role in catalysis field because of its morphology; very thin films with larger surface areas can be very beneficial.

Similarly, in the future, it is recommended to use different solvents or a mixture of various solvents to understand the hydrolysis and condensation process of iron species.

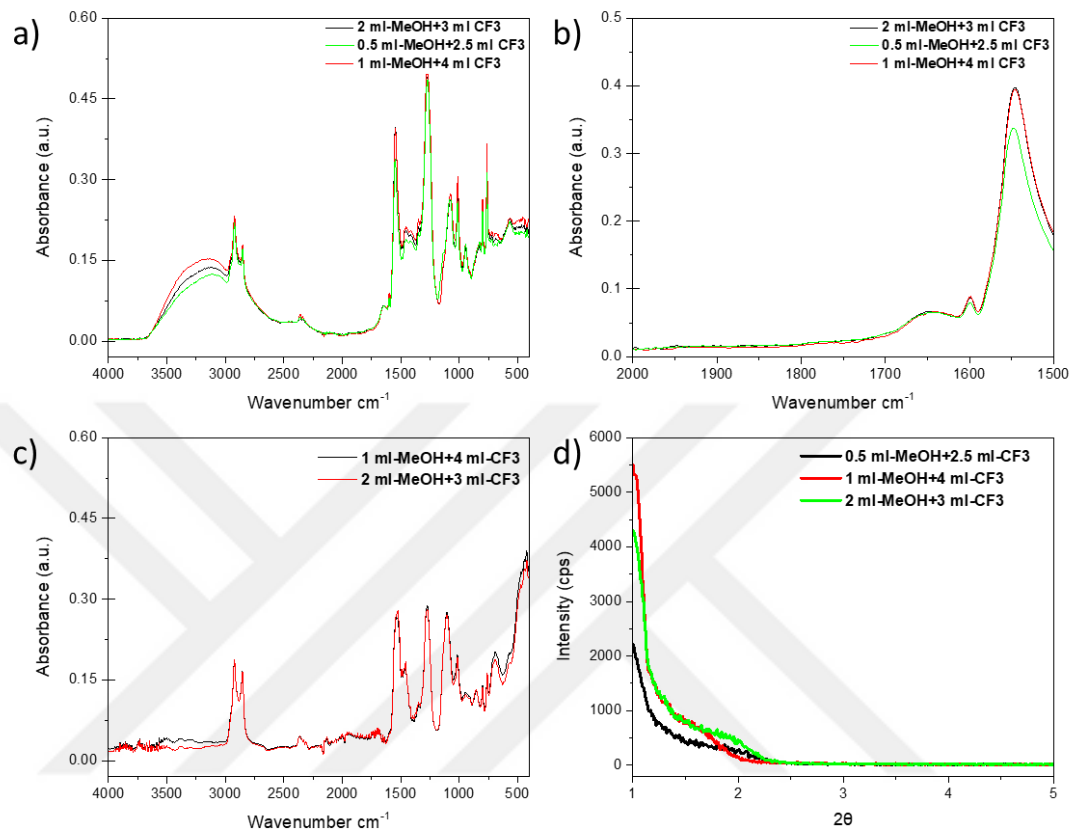


**Figure 5. 1.** (a) & (b) ATR-FTIR spectra of various compositions of TFE and Methanol (c) at 100 °C (d) small angle XRD pattern

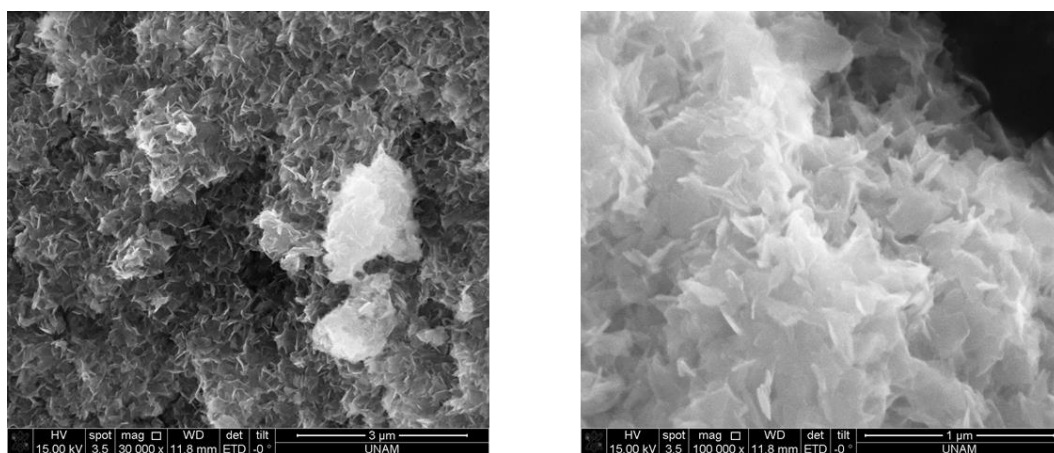


**Figure 5. 2.** SEM Images of Fe<sub>2</sub>O<sub>3</sub> particles using TFE as a solvent

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