

The Formation of Liesegang Patterns of Cobalt Ferrocyanide Prussian Blue Analogue in Polyacrylamide Gels

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF ENGINEERING AND
SCIENCE
OF BILKENT UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF
MASTER OF SCIENCE
IN CHEMISTRY

By
Pedram Tootoonchian

The Formation of Liesegang Patterns of Cobalt Ferrocyanide Prussian Blue Analogue in Polyacrylamide Gels

By Pedram Tootoonchian

January 2022

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

Bilge BAYTEKIN (Advisor)

Burak ÜLGÜT

Ferdi KARADAŞ

Yunus Emre TÜRKMEN

Istvan LAGZI

Approved for the Graduate School of Engineering and Science:

Ezhan KARAŞAN
Director of the Graduate School

ABSTRACT

The Formation of Liesegang Patterns of Cobalt hexacyanoferrate Prussian Blue Analogue in Polyacrylamide Gels

Pedram Tootoonchian

M.S. in Chemistry

Advisor: Bilge BAYTEKİN

January 2022

The formation of patterns in nature has always fascinated scientists who try to understand the mechanism behind this complex phenomenon. Liesegang patterns (LPs) are one category of periodic precipitations patterns formed by the reaction-diffusion (RD) system, studied and modeled by chemists and mathematicians for over a century. The majority of the focus has been on understanding the formation of these patterns, modeling them, and studying the effect of different gel types, gel concentrations, and inner and outer concentrations on various systems. There are only a few examples in the literature showing the effect of temperature, electric or magnetic field, and mechanical force on LPs and controlling the pattern formation by these external stimuli, and more importantly, showing a possible application of these systems. In this work, we show a novel approach to form LPs in a hydrogel medium, track the band formation with temperature, characterize each band, and last but not least, suggest a useful application for these LPs. This study mainly concentrates on the pattern formation of cobalt Prussian blue, but LPs of some other Prussian Blue Analogues (PBAs) are also shown. First, we propose a new method to form PBAs LPs formation. Then, we track the band formation by changing the system's temperature. To understand the effect of temperature on the microscale, we characterize each band using SEM, EDX, and XPS to analyze particles size and Co/Fe ratio. Finally, we use each band as electrocatalysts for water oxidation reactions in water splitting.

ÖZET

Pedram Tootoonchian

M.S. in Chemistry

Advisor: Bilge BAYTEKİN

January 2022

Doğadaki desen oluşumları arkalarında yatan karmaşık oluşum mekanizmaları ile bilim insanlarının ilgisini çekmektedir. Tepkime-difüzyon sistemleriyle (TD) oluşan periodik çökeltme desenlerinden bir grup da Liesegang desenleridir. Bu desenler bir yüzyılı aşkın süredir kimyacılar ve matematikçiler tarafından araştırılmakta ve modellenmektedir. Bu çalışmalarda odak noktası desenleri anlamaya yönelik modellemeler, ve jel tipi ve konsantrasyonu, iç ve dış elektrolitlerin konsantrasyonu gibi değişik parametreler üzerinedir. Yalnız birkaç çalışmada desenler üzerinde ortam sıcaklığının, elektrik ve manyetik alanların ve mekanik kuvvetlerin etkisi çalışılmıştır. Bu çalışmalardan yalnızca bir iki tanesi de desenlerin olası uygulamaları üzerinedir. Bu çalışmada, Liesegang desen oluşumu için yeni bir yöntem gösterilmiştir. Bu yöntemle elde edilen bantların ve bant ürünlerinin içeriklerini karakterize edilmiş, bunlara sıcaklığın etkisi ortaya konmuştur. Çalışmada kobalt prusya mavisi analogları üzerine odaklanılmış sıcaklığın bant oluşumu ve bant ürünlerine etkisi mikro düzeyde SEM, EDX ve XPS ile parçacık boyutu ve Co/Fe oranı sonuçları üzerinden tartışılmıştır. Son bölümde de bant ürünlerinin bir su oksitlenmesi tepkimesinde elektrokatalizör olarak kullanılması gösterilmiştir.

Acknowledgments:

First and foremost, I am highly grateful to be lucky enough to work under supervision of Dr. Bilge Baytekin. Her patience, support, and professionalism have paved my way through the scientific world, and her vision and ideas have been truly valuable and constructive. I am sincerely thankful to her for giving me a free hand in my research, guiding me, and believing in me.

I would like to offer my special thanks to Dr. Joanna Kwiczak Yigitbasi for all her insightful guidance, kindness, and assistance in my experiments and for being a wonderful friend. Also, I am deeply grateful to Turab Ali Khan for introducing me to this work, answering all my questions patiently, and being extremely supportive.

I am thankful to Simay Aydonat for her warm friendship and assistance whenever I needed it. Also, I need to thank my friend Pouria Hasani for his time and support in the experimental device. I appreciate the time and effort of Ramadan Chalil Oglou for the catalysis experiments demonstrated in the final section of this thesis. I would also like to thank all the other former and current group members for making the lab a friendly and welcoming environment.

I would like to thank Dr. Ferdi Karadas for his guidance and support, especially the catalysis part of this project. Furthermore, I highly appreciate the time and help of my other committee members Dr. Burak Ülgüt, Dr. Yunus Emre Türkmen, as well as Dr. Istvan Lagzi.

Last but not least, I am genuinely grateful for having such amazing friends and family, for none of this would be possible without their support.

I acknowledge TÜBİTAK for providing financial support under project no: 219Z263

Table of Contents

1.	Introduction:	1.
1.1.	Theoretical background and modeling.....	3.
1.2.	External stimuli for the control of LPs and temperature as an external stimulus in LP systems.....	6.
1.3.	Prussian Blue (PB).....	8.
1.4.	Prussian Blue Analogues (PBAs).....	10.
1.5.	Liesegang Patterns of PBAs.....	13.
1.6.	The Aim of the Thesis.....	14.
2.	Materials and Methods.....	17.
2.1.	Materials.....	17.
2.2.	The Experimental Method.....	17.
2.2.1.	1D Gels	19.
2.2.2.	2D gels.....	21.
2.3.	Finding the Right Acid and the Right Solvent.....	22.
2.4.	Temperature Control Setup.....	23.
2.5.	Imaging and Analysis.....	25.
2.5.1.	Determination of the Time Law.....	25.
2.5.2.	Spacing Coefficient Analysis (The Spacing Law).....	26.
2.6.	Sample preparation for XPS and SEM.....	27.
2.6.1.	X-ray Photoelectron Spectroscopy (XPS) analysis.....	27.
2.6.2.	Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX) analyses	28.
3.	Results and Discussion.....	29.
3.1.	Optimization of the Concentrations.....	29.
3.1.1.	Characterization of 1-D LPs at Room Temperature.....	31.
3.1.2.	Characterization of 2-D LPs at Room Temperature.....	35.
3.2.	The Temperature Effect.....	36.
3.3.	Other PBAs.....	40.

3.3.1. Copper PBA.....	40.
3.3.2. Fe ^{III} -Fe ^{II} PB.....	41.
3.4. Catalytic Activity.....	43.
4. Conclusion.....	48.
5. References.....	50.



List of Figures

Figure 1: (Left) An example of precipitation patterns in rocks. (Right) Formation of copper chromate Liesegang patterns (LPs) in polyacrylamide hydrogel medium by reaction-diffusion [10]. Diffusion direction is from left to right, bands in the LP are formed with ascending distances.

.....1.

Figure 2: The emergence of a) 1D and b) 2D patterns by the precipitation of copper chromate in PAM hydrogel using WETS technique.....3.

Figure 3: The primary difference between pre- and post-nucleation models. In the pre-nucleation model (a), nucleation and precipitation occur in the same region. However, in the post-nucleation model (b), there is homogeneous nucleation, and precipitation occurs in different regions. Reproduced from [3].....4.

Figure 4: The formation of the Cu^{2+} - Fe^{2+} PBA Liesegang bands in a polyacrylamide hydrogel. The empirical laws are demonstrated on the photo, labeling the position and width of the beige precipitate.....5.

Figure 5: a, b) Tracking the effect of temperature on the LP formation of copper chromate. After 24 hours, Liesegang bands formed at 60 °C have a higher spacing coefficient than those formed at 20 °C. Here, PC represents the point of contact of outer and inner electrolytes in the polyacrylamide hydrogel, and PB represents the precipitation beginning point of copper chromate. The distances between PC and PB decrease by increasing the temperature. c) The particle size of the bands increases with the band number and also by increasing the temperature [10].....8.

Figure 6: The Prussian blue water-insoluble salt formation by mixing the potassium ferrocyanide and iron(III) chloride solutions. 9.

Figure 7: The three-dimensional illustration of PBAs, where M and M' are transition metal ions, and the alkali cation (K^+ or Na^+) fills half of the tetrahedral holes (assuming it is an ideal form).
.....10.

Figure 8: The proposed $4e^-$ proton-coupled electron transfer (PCET) mechanism for electrocatalytic water oxidation with $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA as the catalyst [49].....	12.
Figure 9: The comparison of the conventional and the citrate-based methods to form the LPs.....	14.
Figure 10: (Left) The dimensions of the glass tube used in preparing the 1D gels. (Right) A $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA sample shows acid diffusion to the PAM containing sodium citrate, Co^{2+} , and $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$	20.
Figure 11: (Left) The two-dimensional Plexiglass mold used in the WETS method. (Middle) 3-D printed mold for the preparation of the agarose stamp. (Right) $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA LPs (green) start to form.....	21.
Figure 12: The effect of different solvents used in the acid solution (0.6 M HNO_3) and their volume percents on the pattern formation.....	22.
Figure 13: a) The illustration of the homemade temperature control device using the Peltier element and an Arduino programmed by Python. b) The output diagram of the Python code showing the constant temperature in time (in seconds).....	24.
Figure 14: Time Law plot for a sample of 1D $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA LPs formed at 20 °C through the citrate-based method.....	25.
Figure 15: a) The plot of grey value vs. distance of the bands to the interface of electrolytes using ImageJ analysis. b) The same plot drawn and analyzed by a homemade MATLAB code, i.e., using the 'Findpeaks' function to find the positions of the bands. c) The natural logarithm of the bands' positions vs. the band number. The slope of this plot provides the spacing coefficient of the LP.....	26.
Figure 16: An example XPS survey spectrum of $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA LPs formed by the citrate method showing both cobalt and iron peaks. Three spots for each band are analyzed.....	27.

Figure 17: SEM image analysis of Co ^{II} -Fe ^{II} PBA particles size using ImageJ. Three image spots and around 100 particles in each spot are analyzed for each band. The scale bar represents 30 microns.....	28.
Figure 18: A ‘phase diagram’ demonstrating the relationship between the concentrations of Co ²⁺ and [Fe ^{II} (CN) ₆] ⁴⁻ and the type of precipitation under each concentration condition. Region A= continuous precipitation of Co ^{II} -Fe ^{II} PBA. Region B = Co ^{II} -Fe ^{II} PBA periodic precipitation (LPs) Region C = continuous precipitation of Co ^{II} -Fe ^{II} PBA.....	29.
Figure 19: The space-time evolution of cobalt PB Liesegang patterns using citrate-based method resulting in distinct bands after 168 h.....	30.
Figure 20: The difference between the band and no-band regions in terms of particles shown by SEM images and EDX spectra.....	31.
Figure 21: Examples of XPS survey and HIREs spectra of Co ^{II} -Fe ^{II} PBA LP bands demonstrating cobalt and iron presence in the bands.....	32.
Figure 22: SEM images of Co ^{II} -Fe ^{II} PBA Liesegang bands formed at room temperature and the distributions of particle sizes in each band. The average particle sizes increase as the band number increases (farther from the gel/acid interface).....	33.
Figure 23: SEM images of the cubic particles of Co ^{II} -Fe ^{III} PBA when [Fe ^{III} (CN) ₆] ³⁻ was used as the anion.....	34.
Figure 24: SEM images of 2-D Co ^{II} -Fe ^{II} PBA Liesegang bands at room temperature and their particles size histograms showing the increase in particles size as the distance from the stamp increases. The particles in the bands aggregate and form clusters.....	35.
Figure 25: a) The formation of Co ^{II} -Fe ^{II} PBA LPs at 10, 15, 20, 25, and 30 °C. The PC represents the point of contact of HNO ₃ as the diffusion solution and the PAM hydrogel containing Co ²⁺ , [Fe ^{II} (CN) ₆] ⁴⁻ , and sodium citrate. b) The spacing coefficient increases with the increase in temperature.....	37.

Figure 26: Band bending of Co ^{II} -Fe ^{II} PBA LPs formed at different temperatures. Outward banding for a low temperature and inward bending for a high temperature.....	38.
Figure 27: a) SEM images of the saturated region and the bands 1 to 3 of the Co ^{II} -Fe ^{II} PBA LPs formed at 15 °C and 25 °C as a comparison to analyze the effect of temperature on particles size of Co ^{II} -Fe ^{II} PBA. In front of the SEM images, histograms with the distributions of particles size are shown. b) Average particles size of saturated region and bands 1-5 for the temperature range of 10-25 °C.....	39.
Figure 28: Cu ^{II} -Fe ^{III} PBA pattern formation by citrate-based method.....	41.
Figure 29: Periodic precipitations of Fe ^{III} -Fe ^{II} PB in the acid solution on top of PAM hydrogel using citrate-based method.....	42.
Figure 30: The spatiotemporal evolution of the Prussian blue periodic precipitations in the liquid phase of acid solution due to the periodic swelling of the gel.....	43.
Figure 31: The three-electrode setup for the electrocatalytic water oxidation, in which the cobalt PBA is the working electrode connected to Pt cathode as the counter electrode with an external electric wire, and Ag/AgCl as the reference electrode, all of which immersed in the 0.1 M phosphate buffer solution with pH = 7.....	44.
Figure 32: The cyclic voltammograms showing the catalytic activity of three bands and the saturated region of Co ^{II} -Fe ^{II} PBA LPs for three identically prepared samples. The comparison of the voltammograms and the data acquired and presented in Table 2 shows no correlation of the activity and the band number.....	47.

List of Tables

Table 1: A summary of Hayashi et al.'s studies on PBA periodic precipitation patterns.**13.**

Table 2: Characteristics of each Liesegang band for three samples in terms of particles size, Co/Fe ratio, and the calculated mass of cobalt, based on EDX results, as well as the obtained current at a specific potential per gram of cobalt.**46.**



Chapter 1

1. Introduction

Technology mimics nature in numerous ways, e.g., in soft robotics, biomedical research, and architecture [1] [2]. Pattern formation in trees, rocks (Figure 1 (left)), and skin of some animals – like zebras – has been the source of inspiration for researchers, too; researchers use them to design, form, and explore synthetic patterns [1] [3]. Discovered by the German chemist Raphael. E. Liesegang in 1896, Liesegang Patterns (LPs) are one group of these patterns of reaction-diffusion (RD) in which spontaneous, self-assembled periodic precipitation (PP) bands form [3].



Figure 1. (Left) An example of precipitation patterns in rocks. (Right) Formation of copper chromate Liesegang patterns (LPs) in polyacrylamide hydrogel medium by reaction-diffusion [10]. Diffusion direction is from left to right, bands in the LP are formed with ascending distances.

As shown in Figure 1 (right), LPs synthesized in the laboratory obey a set of mathematical laws; those are the spacing law [4], the time law [3], and the width law [5]. The spacing law governs the distances between consecutive bands. This law is represented as a geometrical series of ascending or descending distances – depending on the type of the reaction front and the chosen precipitation reaction. Most systems follow the ascending geometric series, meaning that

the spacing between adjacent bands increases as the reaction front moves farther from the first band. An example of this type of banding obeying the ascending spacing law can be observed in copper chromate LPs forming in a hydrogel [6]. However, some systems form the descending series—known as revert banding—in which the distance between consecutive bands decreases, in contrast to the regular banding [7]. Mostly, Ag^+ [8] and Pb^{2+} [9] salts form the invert (revert) type of periodic bands.

The Liesegang patterns can form when two water-soluble salts react to form a nearly-insoluble salt in an aqueous medium. The water-containing medium must be dense, where the convection is at its lowest. Keeping the convection at a minimum helps the precipitate form in diffusion control. The classical routine in preparing LP systems is as follows: One reagent is homogeneously dispersed (this reagent solution is called the ‘inner electrolyte’, which I represent here as ‘B’) in a hydrogel. The solution of the other reagent (called ‘outer electrolyte’, which I define here as ‘A’) is let from the top part of the hydrogel. The reaction occurs by the diffusion of the outer electrolyte into the hydrogel and the precipitate forms. LPs have been studied in hydrogels [11], aerogels [12], and even in solids [13], among which hydrogels have been opted for as the best medium to study this phenomenon. Grzybowski’s innovative work in 2005 [14] [15], opened a new chapter in the study of LPs by introducing a new method using gels to contain the outer electrolyte. In this method, known as wet stamping (WETS), the outer electrolyte is also homogeneously distributed inside a hydrogel. This homogeneity is achieved by immersing the stamping gel in the electrolyte solution, which has a higher concentration than the inner electrolyte. Then, the stamp gel containing the outer electrolyte solution is put on top of the previously-prepared inner-electrolyte-containing hydrogel. The WETS technique allows us to investigate 2D patterns, different shaped LPs, and micro- and nanostructured periodic precipitation in reaction-diffusion systems. In Figure 2, the formation of concentric two-dimensional CuCrO_4 LPs is shown.

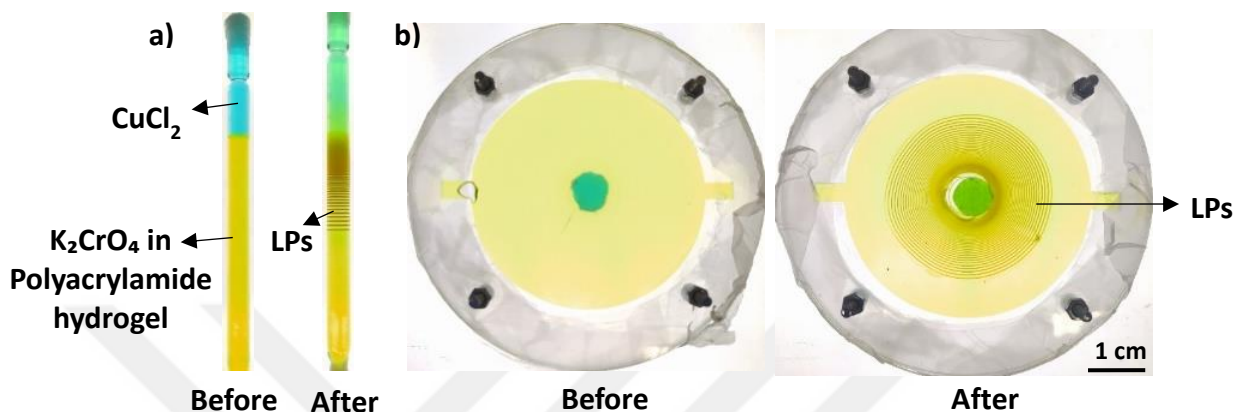


Figure 2. The emergence of a) 1D and b) 2D patterns by the precipitation of copper chromate in PAM hydrogel using WETS technique. *Outer electrolyte (copper(II) ion) = 1 M in solution for 1D and in 8% agarose stamp for 2D, inner electrolyte (chromate ion) = 0.010 M. PAM hydrogel: acrylamide = 12.7 w%, BIS = 0.052 w%, KPS = 0.174 w%, TEMED = 0.0001 w%, $T = 23\text{ }^{\circ}\text{C}$.*

1.1. Theoretical background and modeling

The formation of the LP patterns can be analyzed from the visual clues, and the possible RD mechanism for the observed geometric arrangement of the pattern shapes can be proposed in the form of theoretical models. Since the discovery of the LPs, quite a few theoretical models have been proposed, all of which fall under two categories: *pre-nucleation theory* and *post-nucleation theory* [16] [5] [3] (Figure 3). The models following the former theory all are, in a way, based on the supersaturation model proposed by Ostwald in 1897 [17], suggesting that the precipitate nucleates and the precipitation of bands form when the product of the local ion concentrations of A and B reaches the solubility product (K_{sp}) of that salt, which occurs in the same region of the gel. The nucleation and growth (NG) model [18] is one of the models supporting the pre-nucleation theory. This model claims that by diffusion, $A_{(aq)}$ reacts with $B_{(aq)}$ to form an intermediate $C_{(aq)}$ (when the product of A and B exceeds K_{sp}). By consuming the neighboring A and B, intermediate C grows until it exceeds the second threshold (k'), where

precipitate $P_{(s)}$ nucleates. $P_{(s)}$ can grow by consuming the local C , forming the first band of the LP. The consumption of C creates an 'ion-depleted zone', in which the concentrations of both electrolyte ions are low. Nevertheless, by the continued diffusion, at a farther distance from the depleted zone, once again, the concentrations are high enough to exceed the k_{sp} and (k') , and the second band forms. On the other hand, the post-nucleation model proposes that homogeneous nucleation of the particles is followed by either competitive growth [19] or phase separation [4] [20] but not in the same region.

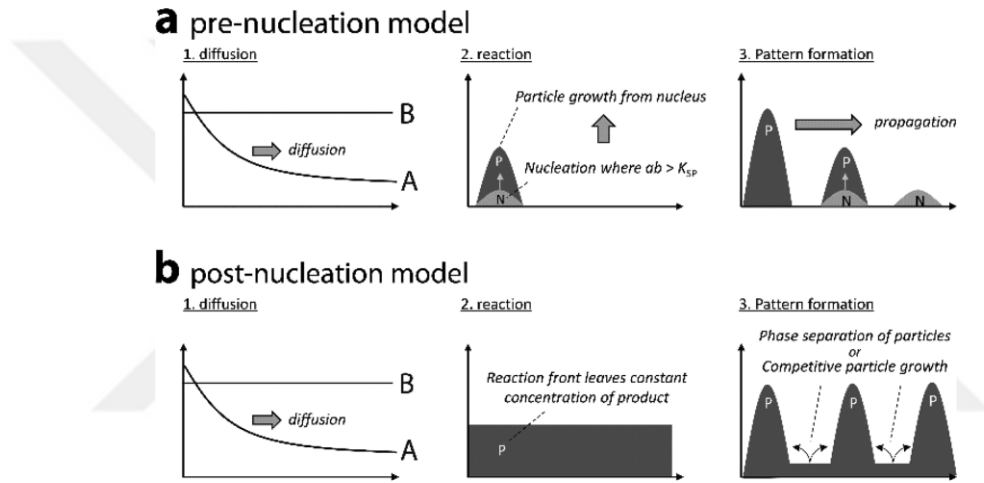


Figure 3. The primary difference between pre- and post-nucleation models. In the pre-nucleation model (a), nucleation and precipitation occur in the same region. However, in the post-nucleation model (b), there is homogeneous nucleation, and precipitation occurs in different regions. Reproduced from [3].

The universal approach to study and compare LP formation uses three empirical equations based on the bands' position, the bands' width, and the time the bands form. These equations are combined to obtain the spatiotemporal analysis of the patterns (Figure 4). The first equation is known as the **spacing law** or Jablczynski law. It states that the distances between consecutive bands x_n and x_{n+1} follow a mathematical pattern. The spacing law equation is described as:

$$\frac{x_{n+1}}{x_n} = 1 + p \quad (1-1)$$

in which $1 + p$ is called the **spacing coefficient**.

The second equation is the **time law** which gives the relationship between the position of the band, x_n , and the time it forms, t_n , which is as follows:

$$t_n \sim x_n^2 \quad (1-2)$$

The following equation can present the periodicity of the width of the consecutive bands:

$$w_n \sim x_n^\alpha \quad (1-3)$$

where α (>1) can be obtained experimentally. Due to the lack of an accurate method to analyze the width of the bands and the fact that the diffusion rate of the outer electrolyte changes the time law, these two latter empirical laws are not very widely used. The spacing law is a standard tool to study the LP formation, and the spacing coefficients $(1+p)$ of LPs are the most commonly reported characteristics of LPs. In 1955, Matalon and Packter [21] stated a direct relation between the initial concentrations of inner and outer electrolyte and the spacing coefficient $(1 + p)$ using the below equation:

$$p = F(b_0) + G(b_0) \frac{b_0}{a_0} \quad (1-4)$$

where F and G are decreasing functions, and a_0 and b_0 are inner and outer electrolytes concentrations. This equation is known as Matalon-Packter law and states that when b_0 is constant, p decreases linearly with a_0 .

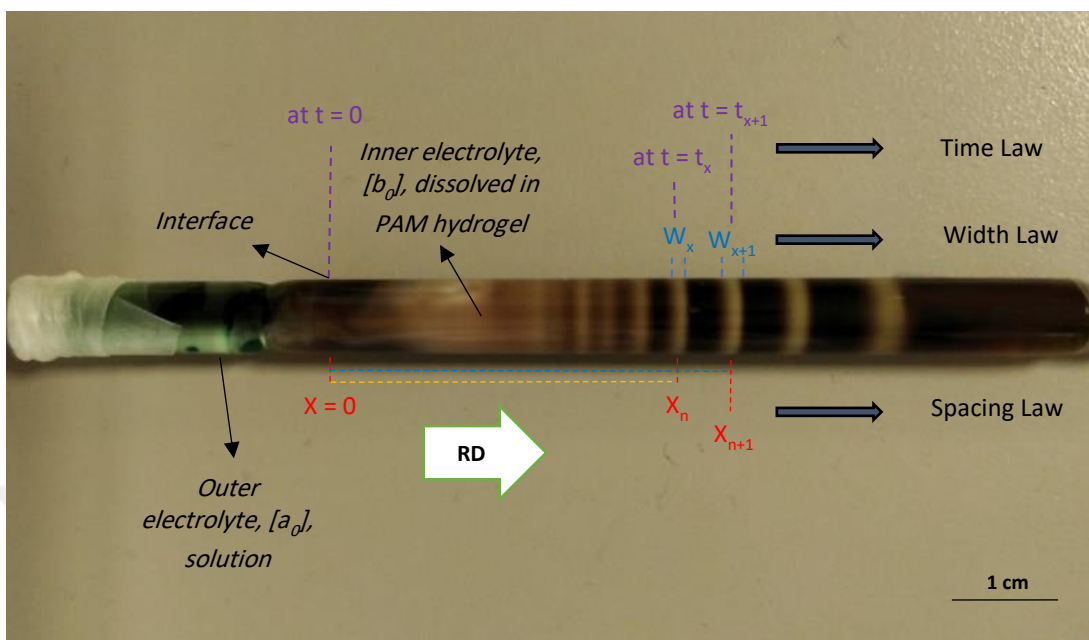


Figure 4. The formation of the $\text{Cu}^{2+}\text{-Fe}^{2+}$ PBA Liesegang bands in a polyacrylamide hydrogel. The empirical laws are demonstrated on the photo, labeling the position and width of the beige precipitate. In this system, potassium ferrocyanide (0.010 M) (brown) in the hydrogel serves as inner electrolyte, and copper ions (the outer electrolyte, green solution) with much higher concentration (1 M) are diffusing from the left.

1.2. External stimuli for the control of LPs and temperature as an external stimulus in LP systems

Liesegang patterns of several precipitates, e.g., CuCrO_4 [6], Co(OH)_2 [22], CaHPO_4 [23], Ag_2CrO_4 [24], are reported in literature. These reports are mostly concentrated on the investigation of the LP formation mechanisms and the effect of different stimuli on the pattern formation, such as electric field [25], magnetic field [26], mechanical stress [27], gravity [28], and temperature [29]. Temperature is of great significance among all the stimuli since it plays a key role in a chemical reaction's thermodynamics and kinetics. The formation of LPs is no exception, meaning that it can be controlled by temperature.

In the 1930s, T. Isemura studied the effect of gel and electrolyte concentrations and the effect of different gels on band formation [30]. In addition, they investigated the effect of

temperature on LPs for the first time. They realized that heating results in fewer bands and larger band intervals [30]. The formation of LPs is determined by the solubility product of the forming salt, the value of which is directly, or in some cases, inversely proportional to the temperature of the environment. The increase or decrease of the solubility product leads to fewer or more bands forming in a given time interval. For example, by decreasing the temperature, we can have more bands in a system forming AgIO_3 , and fewer bands will be formed in the case of Ag_2CO_3 [30]. However, so far, there are no temperature studies of the LP formation in gels at temperatures over 30 °C. The reason for this is a practical one; the LPs so far studied have been mostly in agarose and gelatin, which melt above 40 °C.

In a previous work in our group, we tracked the effect of temperature (ranging from 20 to 60 °C) on the LP formation of CuCrO_4 in polyacrylamide hydrogel (PAM) [10]. The reason why PAM was chosen as the medium in this work was that PAM is a chemically cross-linked hydrogel and has a high glass transition temperature (153-190 °C). Unlike agarose and gelatin, which are only physically cross-linked and therefore melt at lower temperatures, in PAM gels tracking the pattern formation at higher temperatures (40-80 °C) is feasible [31]. This study showed that increasing the temperature increases the spacing coefficient of CuCrO_4 LPs in 1D, 2D, and 3D (in a gel cube). In Figure 5, the 1D LP bands are shown. By comparing the patterns formed at different temperatures (Figure 5a), we can see that the depletion zone is getting wider, and the p of the LPs increases (Figure 5b) as the temperature increases from 20 to 60 °C. In this study, it was also shown that the increase in temperature for this LP system results in the increased solubility product, k_{sp} , of CuCrO_4 and faster diffusion of the outer electrolyte in the gel [32]. Another interesting finding in this work was the greater distance between the point of contact of the outer gel (PC) and the point of precipitation begin (PB) by increasing the temperature. This difference is due to the dissolution of small colloids and aggregation to form bigger colloids at higher temperatures. This phenomenon is reflected in the increasing size of the precipitates of the same generation bands (Figure 5c). The main goal of this thesis is to investigate the effect of temperature on the formation of Prussian blue analogue (PBA) LPs. Prussian blue and its analogues are chemically more complicated solids than copper chromate. CuCrO_4 precipitate has only one chemical species, but in PBA, there can be species with different compositions (vide

infra). Therefore, in an LP system forming PBAs, in addition to obtaining different particles sizes of the precipitates forming in each band, it might be possible to get different composition products in each band - and control all of these with temperature.

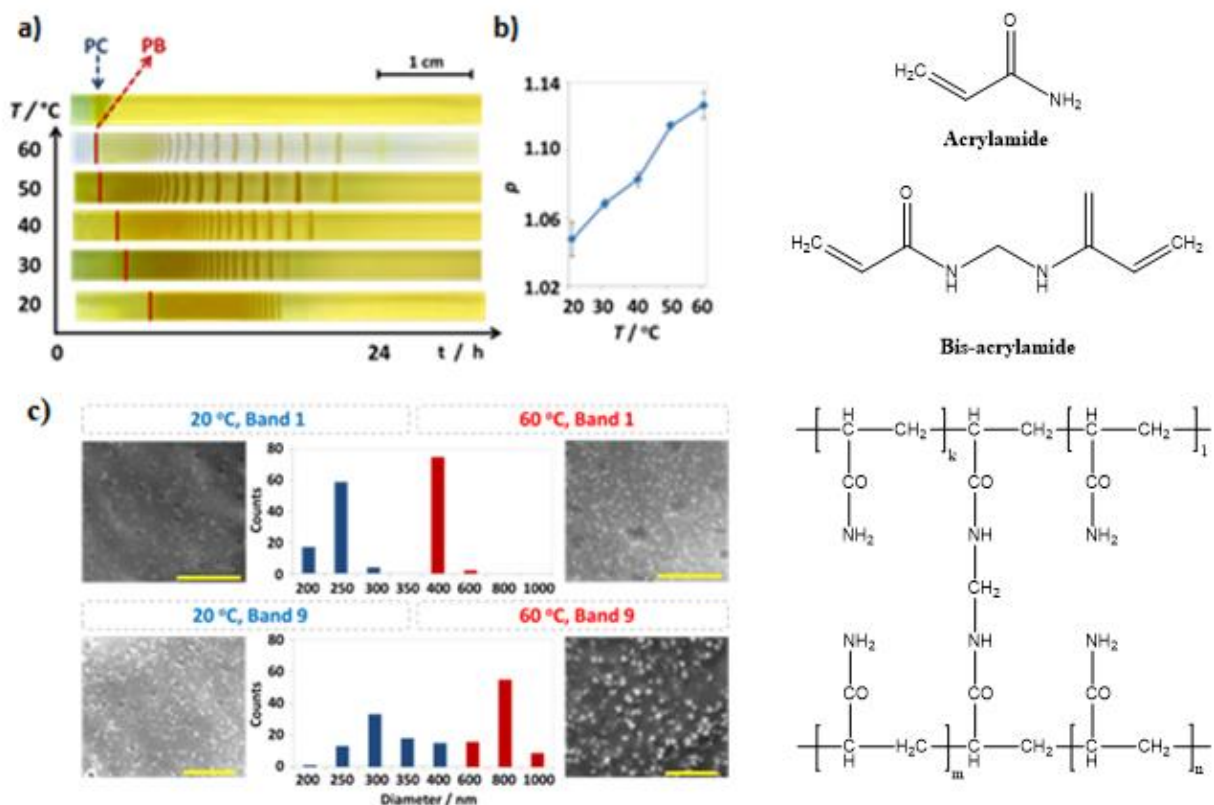
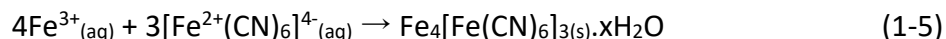


Figure 5. a, b) Tracking the effect of temperature on the LP formation of copper chromate. After 24 hours, Liesegang bands formed at 60 °C have a higher spacing coefficient than those formed at 20 °C. Here, PC represents the point of contact of outer and inner electrolytes in the polyacrylamide hydrogel, and PB represents the precipitation beginning point of copper chromate. The distances between PC and PB decrease by increasing the temperature. c) The particle size of the bands increases with the band number and by increasing the temperature [10].

1.3. Prussian Blue (PB)

It has been almost two centuries since the Prussian blue was first synthesized. Ever since it has attracted researchers due to its interesting coordination structure and numerous applications [33] [34] [35]. This insoluble blue compound comes from the reaction of soluble iron (III) and hexacyanoferrate (II) salts (Figure 6), according to the following reaction:



in which $x = 14-16$. The unique characteristic of this coordination compound is the simultaneous existence of both oxidation states of iron, that is, Fe^{II} and Fe^{III} , in the structure. This type of compounds is known as mixed-valence compounds, and the metal-to-metal intervalence charge transfer (between high-spin Fe^{3+} and low-spin $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$) is responsible for the intense color of the product [36] [37]. Due to non-equivalent stoichiometry ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}} = 4/3$), 25% of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ sites are vacant. This vacancy can be occupied by water molecules coordinated to iron (III) ions. In this case, the structure should be flawed so water could penetrate. The vacancy can also be filled with alkali metal (like K^+ or Na^+) intercalation, acting as counter ions of hexacyanoferrate depending on the synthetic approach used to form the PBAs. The former structures are known as “insoluble” PBs, and the latter products are called “soluble” PBs – which are, in fact, pretty insoluble, but their colloids suspend (colloidal sol) longer in a solution [33] [38]. In an ideal structure, half of the vacancies should be filled with the alkali ion to balance the charge. It is worth mentioning that the same blue compound can be obtained by replacing FeCl_3 with FeCl_2 , which is added to $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ instead of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$. The structure of the product is the same according to the spectroscopic analysis [34] [39]. In both cases, it is found that cyanide acts as a bridge; Fe^{2+} is bonded to carbon, and Fe^{3+} is bonded to nitrogen in the polymeric structure [33].

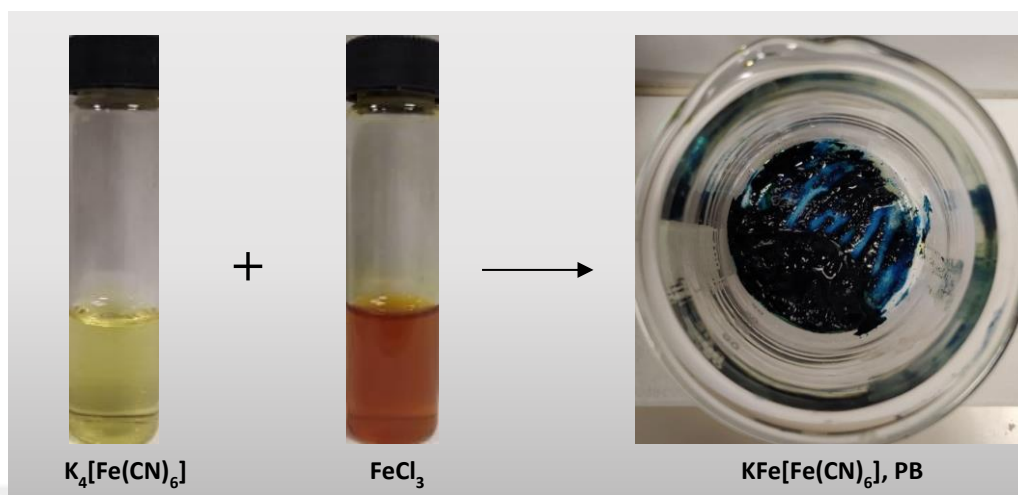


Figure 6. The formation of Prussian blue water-insoluble salt by mixing the solutions of potassium ferrocyanide and iron(III) chloride. This reaction occurs instantaneously.

1.4. Prussian Blue Analogues (PBAs)

The story of Prussian blue is not limited to only iron salts. The ions of 3d-transition metals and hexacyanometallates are perfect choices to synthesize many PB-like compounds, known as Prussian Blue Analogues (PBAs). Same as PB, PBAs are also water-insoluble salts forming from the aqueous reactions of a transition metal ion – such as copper(II), cobalt(II), and manganese(II), to name a few – and a hexacyanometallates ($\text{M}'(\text{CN})_6$, $\text{M}' = \text{Fe}, \text{Co}, \text{Cr}, \dots$) which are both soluble in water [40] [41]. These three-dimensional cubic polymeric cyano-bridged compounds have the general molecular demonstration $\text{A}_y\text{M}[\text{M}'(\text{CN})_6]_x\text{V}_{1-x} \cdot n\text{H}_2\text{O}$, in which A = alkali metal cation, and M, M' = transition metals, and V = vacancy of hexacyanometallate site. Depending on their particle size and morphology stemming from the synthetic approach, PBAs have several potential applications in energy storage [42], as electrodes [43], biosensors [44], and they display photochromism [45] as well as electrochromism [46] [47] [48]. More recently, PBAs were shown to act as water oxidation catalysts (WOCs) for water-splitting [49]. Figure 7 shows the 3D structure of PB and PBA.

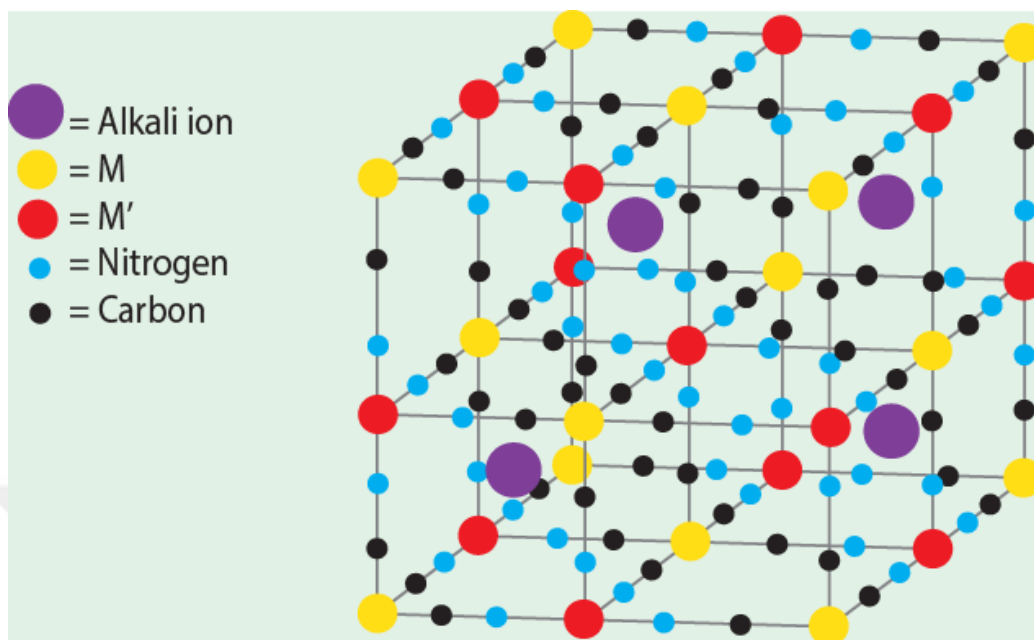


Figure 7. The three-dimensional illustration of PBAs, where M and M' are transition metal ions and the alkali cation (K^+ or Na^+) fills half of the tetrahedral holes (assuming it is an ideal form). Cyanide is the bridging group between the two transition metals in all the PBAs structures. In Co^{II} - Fe^{II} PBA, cobalt ions are coordinated to the nitrogen atoms.

Some possible applications of the PBAs can be summarized as below:

- **Mn-based PBA:** Manganese hexacyanoferrate ($Mn^{2+}-N\equiv C-Fe^{2+}$) and manganese hexacyanochromate ($Mn^{2+}-N\equiv C-Cr^{3+/2+}$) PBAs are metal-organic frameworks (MOFs) with cubic crystals (~ 600 nm, and ~ 2.5 μm , respectively), in which the former can be used as anodes for lithium-ion batteries (LIBs) [50] and the latter can be used as anodes for sodium-ion batteries (NIBs) [51].
- **Cu-based PBA:** Copper hexacyanoferrate (III) nanoparticles can be used as a cathode for NIBs due to their high electrochemical stability [52]. In addition, they can be used in drug delivery in cancer therapy [53].
- **Ni-based PBA:** Ni-Fe PBAs have applications in oxygen evolution reaction (OER) as catalyst [54], energy harvesting [55], H_2O_2 sensors, as well as electrochromic materials [56].
- **Co-based PBA:** Cobalt hexacyanoferrate (with the formula $A_xCo_y[Fe(CN)_6] \cdot zH_2O$, A = alkali cation) is a promising catalyst for water oxidation reactions in water splitting due to the

high abundances of the precursors involved in making the catalyst material, simple synthesis method, and fast electron transfer [49] [57]. Water splitting is an endothermic decomposition of water into oxygen and hydrogen according to the following reaction:



The electrochemical water splitting is two simultaneous reactions, each in a half cell. One is the oxygen evolution reaction (OER), water oxidation at the anode electrode (1-7), and the other is the hydrogen evolution reaction (HER) at the cathode electrode (1-8).



This means we need one catalyst for water oxidation and one for proton reduction. The major challenge in water splitting is water oxidation because of the number of electrons transferred in this half-reaction. Cobalt hexacyanoferrate PBAs can be a suitable WOC to overcome the energy barrier of water oxidation by lowering the activation energy of the reaction. In the $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA structure, cobalt is the catalytically-active site ($\text{Co}^{2+/3+}$ redox), and iron is inactive as electrocatalyst and acts just as an electron donor to feed electrons to the cobalt redox reaction [49]. In Figure 8, a 4e^- mechanism for the catalysis is proposed, known as proton-coupled electron transfer (PCET), where high-valent cobalt, as the active site, is attacked by water, leading to the release of O_2 . One main reason cobalt PB is a quality electrocatalyst is that the surface concentration of cobalt as an active site is enhanced, and owing to $\text{C}\equiv\text{N}$ bonds, the distance between two adjacent cobalt sites is increased.

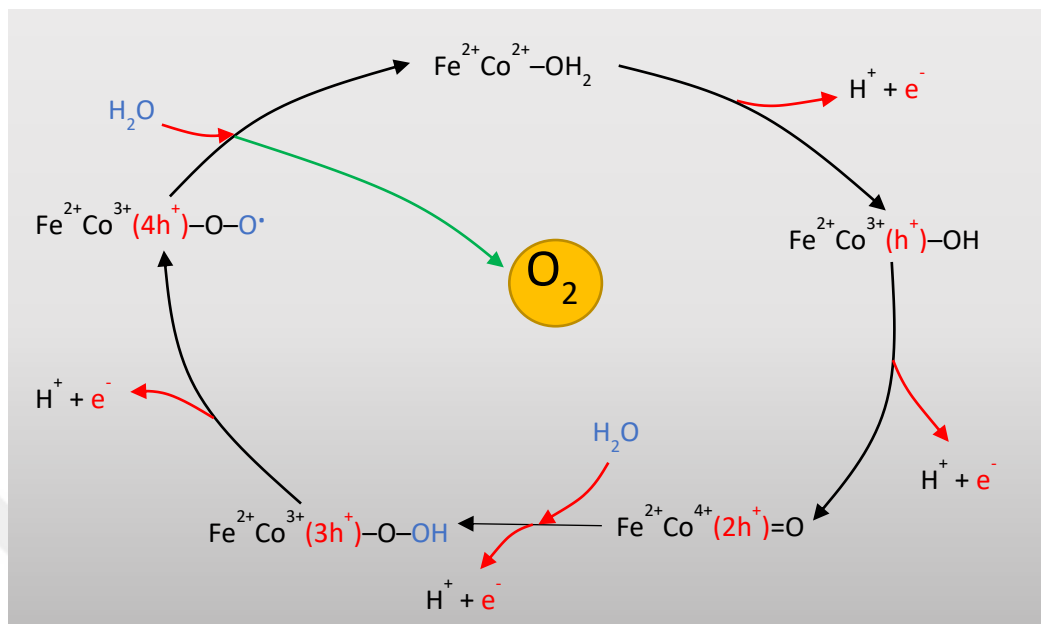


Figure 8. The proposed $4e^-$ proton-coupled electron transfer (PCET) mechanism for electrocatalytic water oxidation with $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA as the catalyst [49].

1.5. Liesegang Patterns of PBAs

There are only a few studies on PBAs LPs in the literature, all done by the Hayashi group. Hayashi et al. have reported the formation of Mn-Fe PBA [58], $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA [59], and more recently, Cu-Fe PBA [60] Liesegang bands in different hydrogel media. Mn-Fe-based PBA Liesegang bands were shown application as a pulsatile ^{137}Cs absorbent from seawater (due to irreversibility of the reaction) [61]. A summary of PBA Liesegang patterns studies by Hayashi is shown in Table 1. In this thesis, I will mention their approach to form LPs as the '**conventional method**', i.e., the diffusion of the metal ion solution of one electrolyte (outer electrolyte) into the other metal ion (inner electrolyte) inside the hydrogel media. In addition to this conventional method, for $\text{Cu}^{\text{II}}\text{-Fe}^{\text{II}}$ LPs, they came up with a novel synthetic method (known as reaction-diffusion-reaction (RDR)) using cyclic voltage, where the electrochemical reaction to form ions, the electric-field-induced diffusion of the ions, and the precipitation reactions are coupled to form LPs. Various patterns can be formed in this system, changing the ions' concentrations by

altering the applied voltage. However, the drawback of this approach is that the bands do not follow the LPs law, and they form stochastically.

<i>PBA</i>	<i>Characterization</i>	<i>Method</i>	<i>Application</i>	<i>Reference</i>
$Mn^{2+}-Fe^{2+}$	• XRF • XANES • SEM	conventional	• pulsatile ^{137}Cs absorbent • potential application as micro-magnetic and electrode array by self-assembly	[61]
$Cu^{2+}-Fe^{2+}$	• XRF • SEM	reaction-diffusion-reaction (RDR) using electric field	-	[60]
$Co^{2+}-Fe^{2+}$	• XRF • XANES	conventional	• potential application in pulsatile drug delivery • potential application as magnets	[59]

Table 1. A summary of Hayashi et al.'s studies on PBA periodic precipitation patterns.

This thesis work introduces a new approach for forming PBAs LPs using a capping (chelating) agent, trisodium citrate. In this method (I will call it '**citrate-based method**' from now on), both electrolytes are in the gel medium containing sodium citrate. The chelate binds to the metal ions (Co^{2+} and Fe^{2+} in $Co^{II}-Fe^{II}$ PBA), preventing the immediate reaction with each other. In a 1D setup, an inorganic acid solution is subjected to the top of the gel to start the precipitation reaction. The acid diffuses into the gel, reacts with citrate to release the ions, and the ions begin to react with each other to make PBAs Liesegang bands (Figure 9) [62] [63].

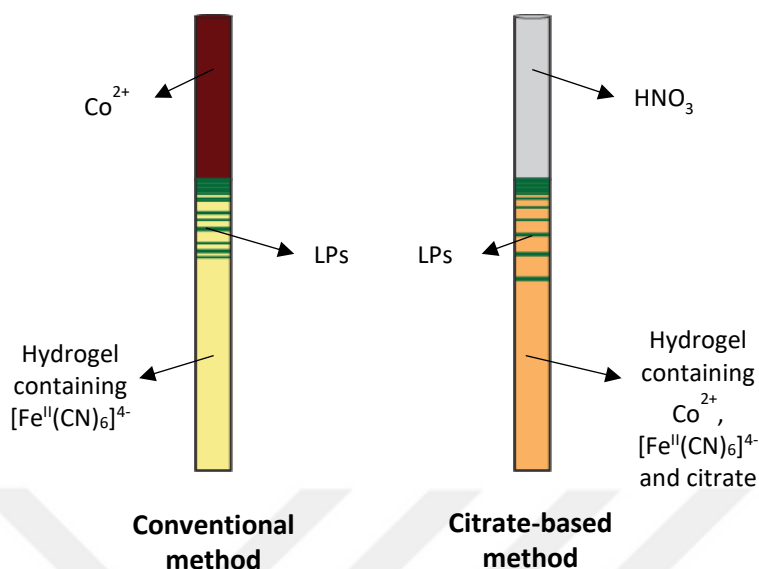


Figure 9. The comparison of the conventional and the citrate-based methods to form the LPs. In the citrate-based method, the bands form sooner (two weeks of the conventional method vs. 3-4 days of the citrate-based method), obey the empirical laws, and are more distinct, making it a better approach to form $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA LPs.

The Liesegang pattern formation using the citrate-based method has also been successful for $\text{Fe}^{\text{III}}\text{-Fe}^{\text{II}}$ Prussian blue and $\text{Cu}^{\text{II}}\text{-Fe}^{\text{III}}$ PBA. However, the main focus of this thesis will be on cobalt PBA LPs.

1.6. The Aim of the Thesis

The LPs have been studied for the interesting mechanism behind the pattern formation process. As summarized in the previous sections, several mechanisms are proposed through experimental and theoretical work, and different stimuli have been probed to find their effect on the LP formation. However, there are very few studies on a practical application with LPs. This scarcity is interesting, since

1) these patterns often offer good control over spatial organization/patterning of matter at the macro level that might have applications in, e.g., sensor and electronics [64],

2) the preparation of materials with LP formation offers a 'set' of products, which often have different distributions of particle sizes owing to the nature of the RD processes that lead to these differences.

In the literature, the LP products in the different band generations of the LP systems are chemically equivalent since they are made up of a cation and an anion. There are only a few examples of chemically different products obtained in the different generation bands of the same pattern. One example is where different lengths of organic polymer chains are formed through the reaction of monomers upon diffusing the initiator [65], and the other is the report on the LP PBA bands [60]. As shown above, I concentrated on the $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA bands in this work since they have many different potential applications. **My aims are;**

- 1) to find a practical synthetic approach to obtain $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA LPs**
- 2) to inspect and identify the product in each band of each pattern in a $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA LP system,**
- 3) to show a way to control the identity and particles size of the products by using the straightforward input of temperature.**

In the final part of this text, I discuss a preliminary test of the formed LP products as a water oxidation catalyst.

To study the products in the PBA LP systems, I first needed to develop a practical synthetic approach for forming $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA Liesegang patterns in polyacrylamide hydrogels. In the literature, synthesis of $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA bands takes more than two weeks, and they do not follow the LPs laws. With our citrate-based method that I invented, the bands form in 3-4 days, and they obey the three empirical laws of LPs. The bands also form more distinctly, which enabled us to use SEM, EDS, as well as XPS for the characterization of the precipitation product in each band. The characterization of these products in each band is more than a chemical identification but an essential analytical part for the performance comparison of the products. Therefore, I aim at precise particle size characterization with SEM and elemental characterization with EDS and XPS.

The effect of temperature on the pattern formation is studied by the LPs in gels formed at different temperatures (10-25 °C). Finally, the catalytic activity of each band as WOCs in oxygen evolution reaction (OER) is inspected by a catalysis setup similar to the one reported in [49].



Chapter 2

2. Materials and Methods

2.1. Materials

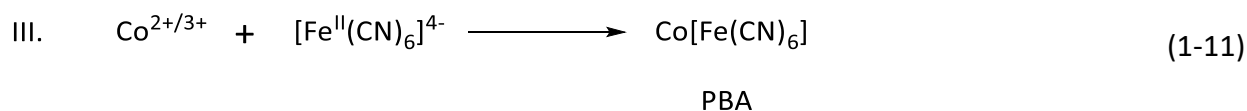
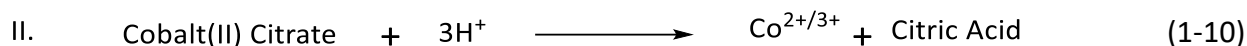
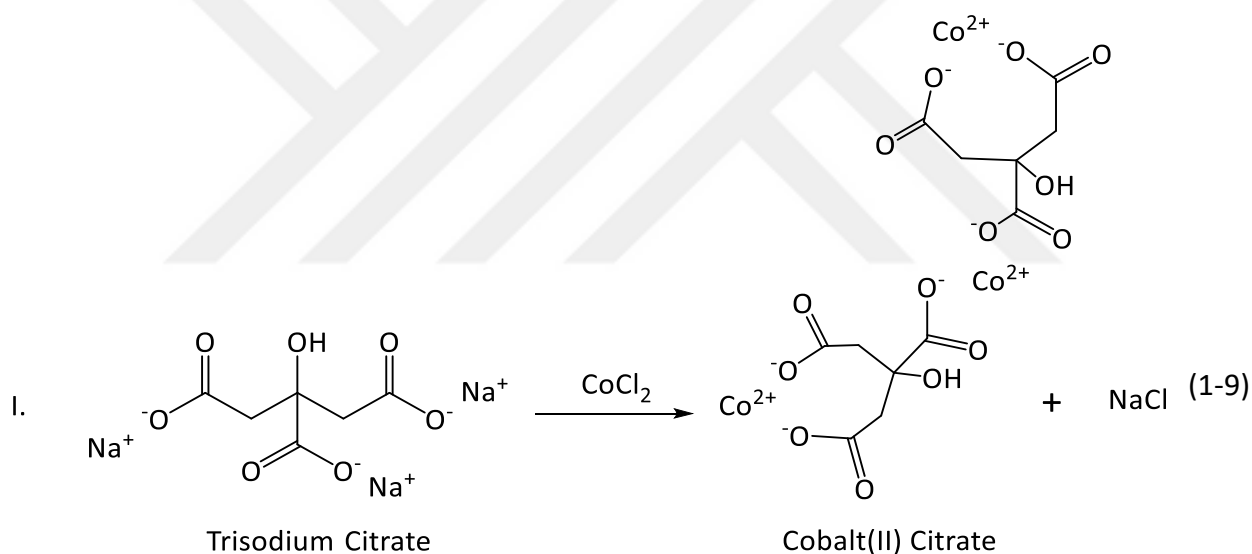
Acrylamide (AA) (Sigma-Aldrich, 98 % purity), N,N'-methylene(bis)acrylamide (BIS) (Sigma-Aldrich, 99% purity), potassium peroxydisulfate (KPS) (Sigma-Aldrich, 99% purity), N,N,N',N'-tetramethylethylene-diamine (TEMED) (Sigma-Aldrich, 99% purity), agarose (Fisher Chemical), cobalt(II) chloride hexahydrate (Fisher Chemical, 96.5% purity), potassium ferrocyanide trihydrate (AFG Bioscience), potassium ferricyanide (AFG Bioscience), trisodium citrate dihydrate (Sigma-Aldrich), nitric acid (Sigma-Aldrich, 65%), copper(II) chloride dihydrate (Acros Organics, 98% purity), iron (III) chloride tetrahydrate (Sigma-Aldrich).

Plexiglass and Parafilm® were used without any chemical modification.

2.2. The Experimental Method

The formation of distinct Liesegang bands depends on multiple factors, including the diffusion coefficient of the outer electrolyte into the hydrogel, the degree of cross-linking, the reaction rate, the gel concentration, and the concentrations of inner and outer electrolyte. Hayashi et al. used agarose and water-glass hydrogels as the medium in which the PBAs LP bands form. In these media, the band formation took more than two weeks. The reason for the prolonged LP formation could be both the low diffusion coefficient of the outer electrolyte (Co^{2+} , Mn^{2+} , or Cu^{2+}) into the gel and the slow rate of the reaction of inner and outer electrolyte to form the PBA. In their case, the patterns formed did not obey the LP equations. Finally, the pattern bands were closely spaced, making the separation and characterization of the products in each band difficult. Therefore, we propose a citrate-based preparation method for the PBA LPs to form faster, in 70-80 hrs. This method also yields distinct patterns, which are easier to analyze the products forming in the bands. In this method, both electrolytes are in the gel medium, and a 'releasing agent' (acid solution) diffuses from the top. To prevent the two electrolyte ions from

reacting with each other, initially, trisodium citrate is added as a chelating agent inside the pre-gel solution to trap the cation, e.g., Co^{2+} (1-9) [64], so that there is no reaction with ferrocyanide (or ferricyanide for the synthesis of $\text{Fe}^{\text{III}}\text{-Co}^{\text{II}}$ PBA), which is added subsequently. Then, after the gelation with TEMED, a strong acid is added from the top of the gel. The acid diffuses and reacts with cobalt citrate, which releases Co^{2+} ions (citric acid is produced as a byproduct (1-10)). The released ions react with $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ ions to form the green Prussian blue analogue ($\text{K}_x\text{Co}_y[\text{Fe}(\text{CN})_6]_z$) (1-11). The exact chemical formula of the PBA in each band can be different in terms of cobalt and iron oxidation states because some of these ions oxidize due to the diffusion of acid (will be discussed more in section 3.4.).



The emergence of periodic precipitation (and not just continuous precipitation) required a lot of optimization. (I got a lot of grey hair during the process but kept on smiling.) The degree of cross-

linking of the hydrogel, the gel thickness, the concentrations of the electrolytes, the concentration of sodium citrate, and the molarity and kind of the diffusing acid had to be optimized since they affect the band formation. The experimental data given below is for the optimized processes.

2.2.1. 1D Gels

For one-dimensional LP, glass tubes were used. The tubes were 10 cm long and 5 mm in diameter. About two-third (7 cm) was filled with the gel, and the rest was filled with the acid after gelation (Figure 10). To make the gel, 1.46 g of acrylamide (the monomer), 0.02 g of KPS (the radical initiator), and 0.006 g of BIS (the cross-linker) were ultrasonicated for 5 minutes in 7 mL of water and 3 mL of 1 M trisodium citrate (10 mL solution in total). It was found out that the pH for this process should be around 8 for the bands to form. Then, the solution was divided into five beakers, each containing 2 mL, using a micropipette. To each beaker, 30 μL of 1 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (to make 0.015 M of Co^{2+}) and 40 μL of 0.5 M $\text{K}_4[\text{Fe}^{\text{II}}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ (to make 0.010 M of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$) were added, and the mixture was stirred for 2 minutes for homogeneity. In the end, 10 μL of TEMED (the catalyst) was added to each beaker, and after stirring for 10 seconds, the solution was transferred to the glass tube using a 5 mL syringe. The sample was left for gelation for almost 24 hours. Then, a solution of 0.6 M HNO_3 (25% of which contains DMF) was subjected to the hydrogel from the top of the glass tube, and the tube was closed using Parafilm. The reason for using DMF is that it dissolves all the material in the system (except for ferrocyanide and PBA forming) and yields a sooner pattern formation.

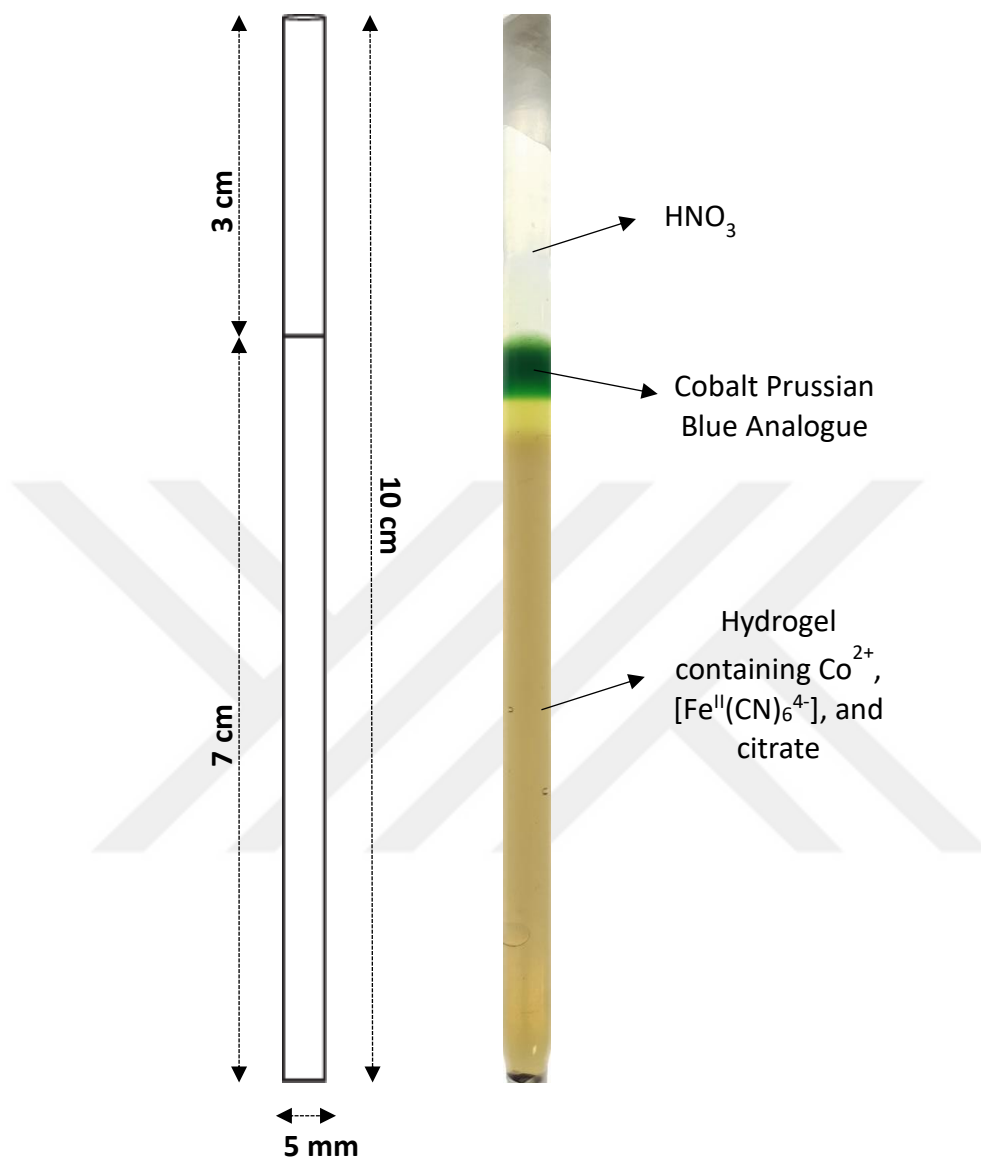


Figure 10. (Left) The dimensions of the glass tube used in preparing the 1D gels. The tube is 10 cm long and 0.5 cm in diameter. Two-third of the tube is filled with gel and one-third with the acid solution. (Right) A Co^{II}-Fe^{II} PBA sample. Acid diffuses in the PAM containing sodium citrate, Co²⁺, and [Fe^{II}(CN)₆]⁴⁻. For further details on concentrations, see Section 2.2.1.

2.2.2. 2D Gels

For two-dimensional LPs, the wet-stamping (WETS) method was used. Round-shaped molds of Plexiglass with an inner radius of 3.5 cm were cut using a laser cutter. There is a spacer mold sandwiched between two Plexiglass pieces in this design, one of which has a round-shaped 1 cm hole in the middle where the stamp is put (Figure 11). For the gel, 1.46 g of acrylamide (the monomer), 0.02 g of KPS (the radical initiator), and 0.006 g of BIS (the cross-linker) were ultrasonicated for 5 minutes in 7 mL of water and 3 mL of 1 M trisodium citrate (in total 10 mL solution). Then, 150 μL of 1 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (to make 0.015 M of Co^{2+}) and 200 μL of 0.5 M $\text{K}_4[\text{Fe}^{\text{II}}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ (to make 0.010 M of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$) were added, and the mixtures were stirred for 2 minutes, to obtain homogeneous solutions. After that, 30 μL of TEMED (the catalyst) was added to the solution, stirred for 10 seconds, and then transferred to the mold by a 10 mL syringe. The sample was left for gelation for 24 hours. For the stamp, a cylinder of 8% agarose, 1 cm diameter and 0.75 cm height, was let in the acid solution (0.6 M HNO_3 (25% of which contains DMF)) for 2 hours. After drying with a tissue, the stamp was placed on the hydrogel, and the whole system was sealed with a piece of Parafilm.

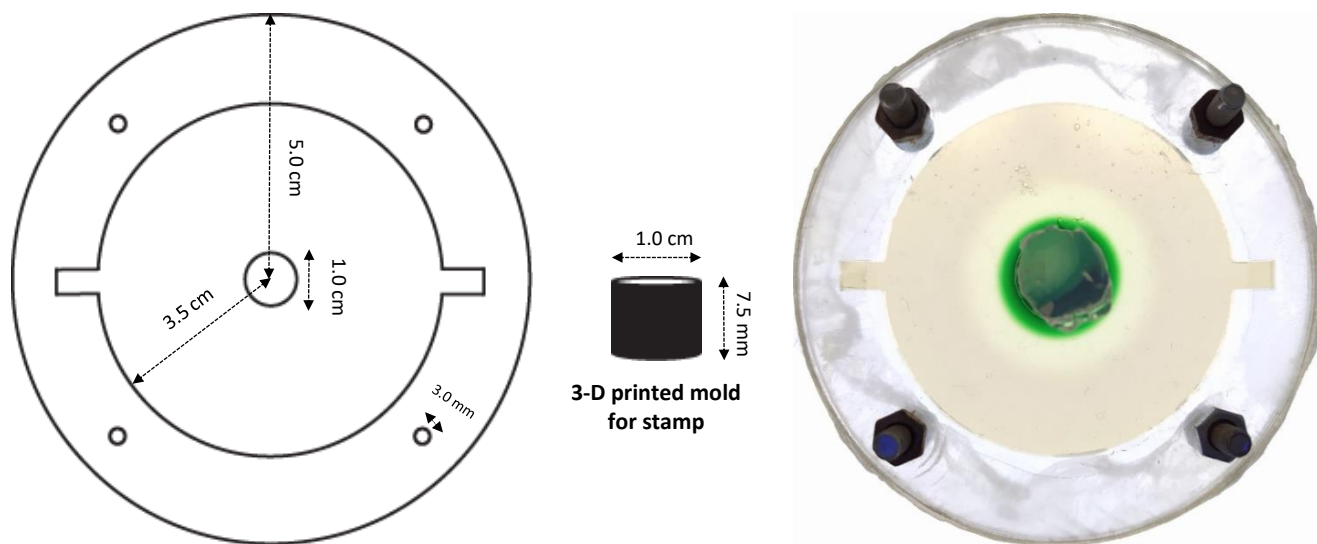


Figure 11. (Left) The two-dimensional Plexiglass mold is used in the WETS method. (Middle) 3-D printed mold for the preparation of the agarose stamp. (Right) $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA LPs (green) start to form with agarose stamp pre-soaked in the 0.6 M HNO_3 in 25% DMF solution is placed at the top and in contact with the hydrogel containing electrolytes and citrate solutions. For further details on concentrations, see Section 2.2.2.

2.3. Finding the Right Acid and the Right Solvent

To obtain visually and mathematically the best LP patterns, the type of strong acid, its ideal concentration range, and the solvent for the acid solution had to be optimized. For the acid, HNO_3 , HCl , H_3PO_4 , and H_2SO_4 were chosen, and aprotic solvents like DMF, DMSO, and 1,4-dioxane with different volume-percents in water were selected. For each solvent, three different molarities of each acid (0.3, 0.6, and 1 molar) and five different volume percents of the solvent in water (10, 25, 50, 70, 90 %) were probed. Based on the visual observations, all the chosen acids provide almost similar LPs but at different times; 0.6 M nitric acid forms the bands faster than the other ones. However, the type of solvent of the HNO_3 solution and the volume percent significantly affect the bands' formation (Figure 12). It turns out that 25% v/v DMF results in more bands obeying the LPs empirical laws in a shorter reaction time.

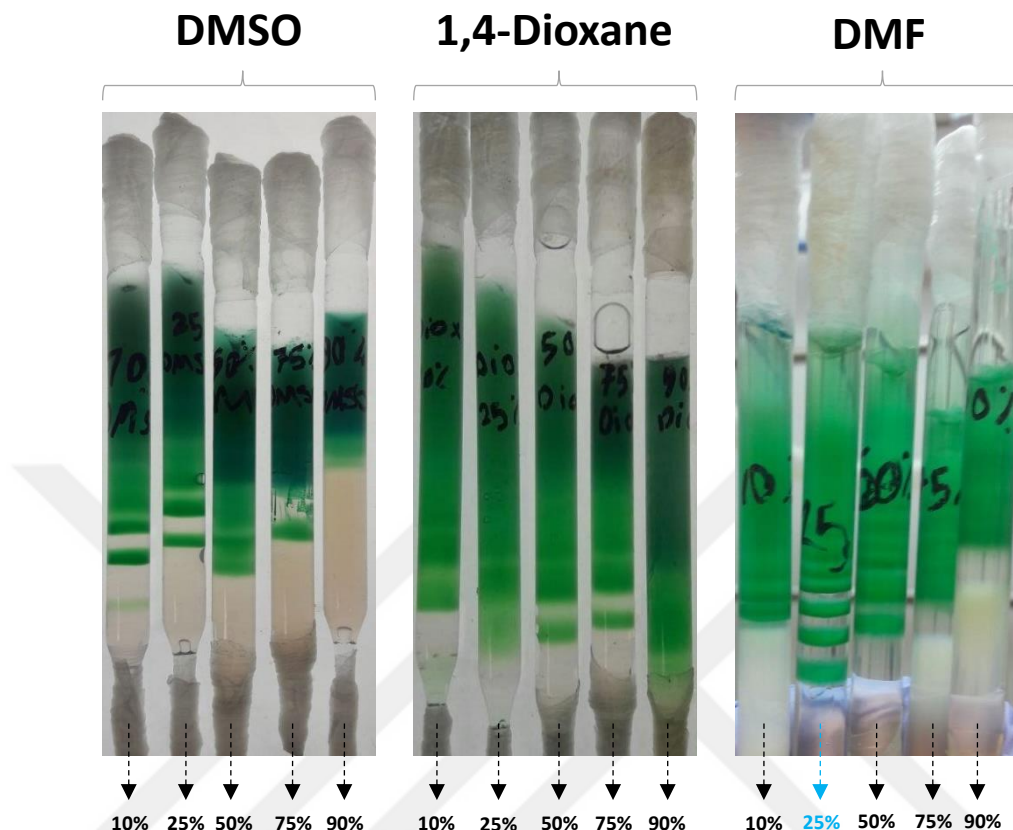


Figure 12. The effect of different solvents used in the acid solution (0.6 M HNO_3) and their volume percents on the pattern formation. The most proper solvent is DMF in the nitric acid solution when the volume percent is 25 %v/v. The bands follow all the empirical laws of Liesegang patterns. In the hydrogel, $[\text{Co}^{2+}] = 0.015 \text{ M}$, $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-} = 0.010 \text{ M}$, and $[\text{sodium citrate}] = 0.3 \text{ M}$ for all cases.

2.4. Temperature Control Setup

A homemade device was used for controlling the temperature. The device set (Figure 13) used a Peltier controlled by Arduino Uno. The device is based on the Peltier effect (thermoelectric cooling). It can be programmed to cool and also to heat. The Peltier element used in our experiment is TEC1 12715 Peltier Cooler, the maximum voltage and current of which is 15V and 15A, respectively, and is mounted on a heat sink (HYPER TX3 EVO). A thin layer of thermal compound (paste) is applied to both sides of the Peltier to increase the conductivity. Then, an aluminum plate is placed on top of the Peltier. For the thermocouple sensor, we used a K-type

thermocouple sensor, which works in the range of -20 to 80 °C (with the temperature sensitivity of 0.25 °C); one end of which is sandwiched between the aluminum plate and a piece of Plexiglass so that there is no disconnection, and the other end is connected to the Arduino Uno using MAX6675 chip to process the voltage information obtained from the difference of temperature of Arduino and the Peltier. For programming of the desired temperature, the Arduino Uno is connected to Spyder Python. There is also a Peltier Driver (BTS7960B 40 Amp DC Motor Driver) that gets the output of MAX6675 (after PID controller loop in Arduino) to drive the Peltier element. This motor driver can work up to 28V.

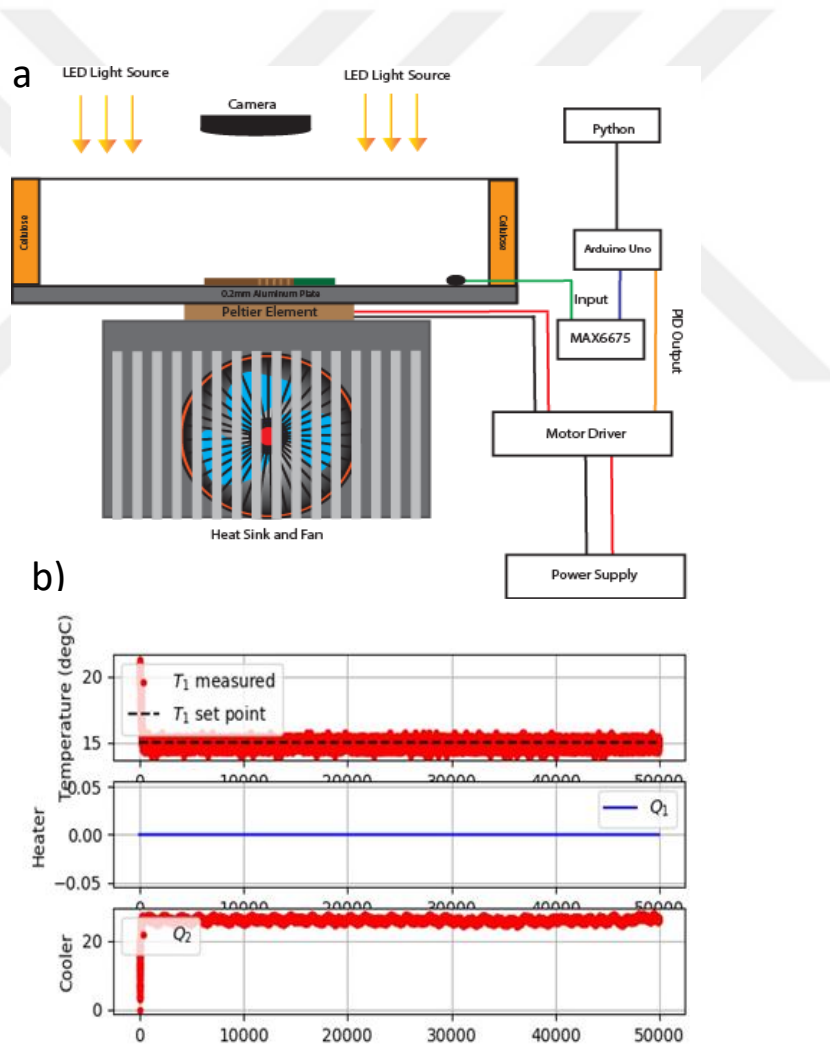


Figure 13. a) The illustration of the homemade temperature control device using the Peltier element and an Arduino programmed by Python. b) The output diagram of the Python code shows the constant temperature in time (in seconds).

2.5. Imaging and Analysis

2.5.1. Determination of the Time Law

We reported the time at which each band appears to compare the differences of the effect of external stimuli on the bands. To do so, we used a Canon EOS 250D 18-55mm to take consecutive photos of the LP forming PAM gel with 30 min intervals for the Co^{II} - Fe^{II} PBA system. Then, by using ImageJ, we draw a line from the interface of the outer and inner electrolyte (inside the hydrogel) to each band to find out the exact position of the bands. In the end, according to the (1-2) formula, a diagram is plotted to show the relationship between the position of bands and the square root of time for them to form (Figure 14).



Figure 14. Time Law plot for a sample of 1D Co^{II} - Fe^{II} PBA LPs formed at 20 °C through the citrate-based method. $[\text{Co}^{2+}] = 0.015 \text{ M}$, $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-} = 0.01 \text{ M}$, and $[\text{sodium citrate}] = 0.3 \text{ M}$ in the hydrogel is subjected to 0.6 M HNO_3 (in 25% DMF). The plot represents the linear relationship between the position of the bands and the square root of the time taken for them to form.

2.5.2. Spacing Coefficient Analysis (The Spacing Law)

To investigate the position of bands and the spacing coefficient as a factor to compare LPs, ImageJ and MATLAB software were used. By drawing a straight line on the sample image in

ImageJ (the image taken by the above-mentioned Canon camera system), a gray value profile based on red, green, and blue (RGB) colors is plotted using $\text{gray} = 0.299\text{red} + 0.587\text{green} + 0.114\text{blue}$ formula. In this plot, each peak represents a band in our LP, and the x-axis provides the position of the bands with respect to the solutions' point of contact) in pixels (Figure 15a). We insert this plot in a home-written MATLAB code to find the peak positions (X_n) (Figure 15b). The spacing coefficient ($X_{n+1}/X_n = 1 + p$) can be found as the slope of another plot in which the natural logarithm of the peak position is plotted against peak number (Figure 15c). In addition to the spacing coefficient, the prominence (the intensity of each peak) and the width of each band can also be studied using the built-in "Findpeaks" function of MATLAB code.

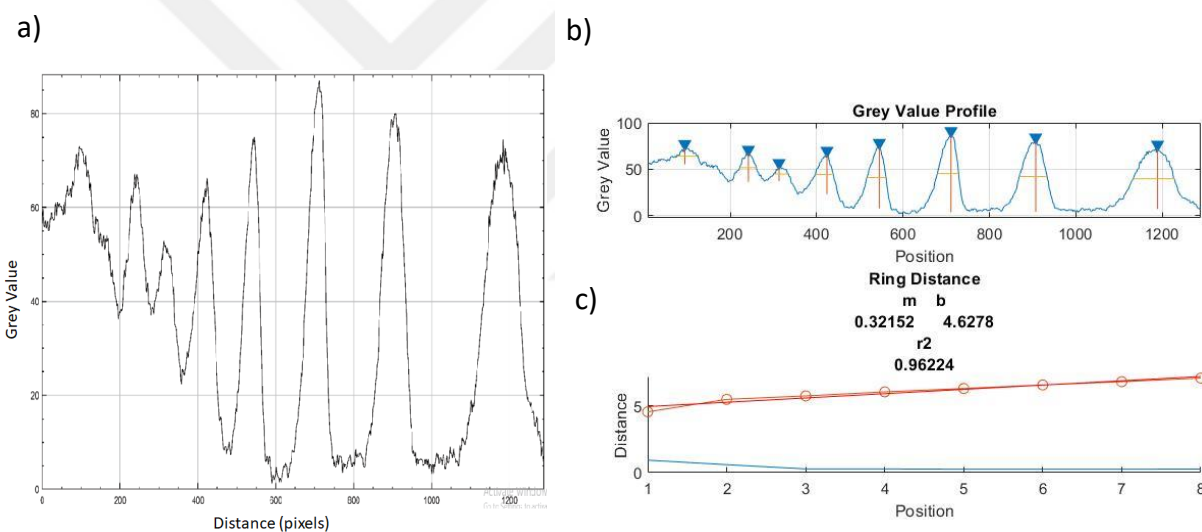


Figure 15. a) The plot of grey value vs. distance of the bands to the interface of electrolytes using ImageJ analysis. b) The same plot drawn and analyzed by a homemade MATLAB code, i.e., using the 'Findpeaks' function to find the positions of the bands. c) The natural logarithm of the bands' positions vs. the band number. The slope of this plot provides the spacing coefficient of the LP.

2.6. Sample preparation for XPS and SEM

To study the bands' composition, particles size, and morphology, XPS and SEM-EDX were used. Since the sample's surface might be contaminated, we cut each band region of the gel in half to analyze the cross-section. We put the whole sample in a glass flask after taking it out of the glass tube (1D) or the plexiglass mold (2D) and freeze dry the sample for 15-30 minutes using

a vacuum chamber and liquid nitrogen. Then, the sample is transferred to a metal plate, and we cut each band in the sample immediately using a clean and sharp blade. After that, each band is also cut in half to analyze the inner surface. We then transfer all the cut pieces to a Petri dish and place the dish in vacuum for at least 24 hours.

2.6.1. X-ray Photoelectron Spectroscopy (XPS) analysis

For XPS, the samples prepared from each band are mounted on copper tapes to increase the conductivity. Thermo Scientific K-alpha XPS instrument using an ion etch with 2000Kv was used. XPS spectra from three spots were measured for each band, and the elemental analysis was done using the instrument software (Figure 16).

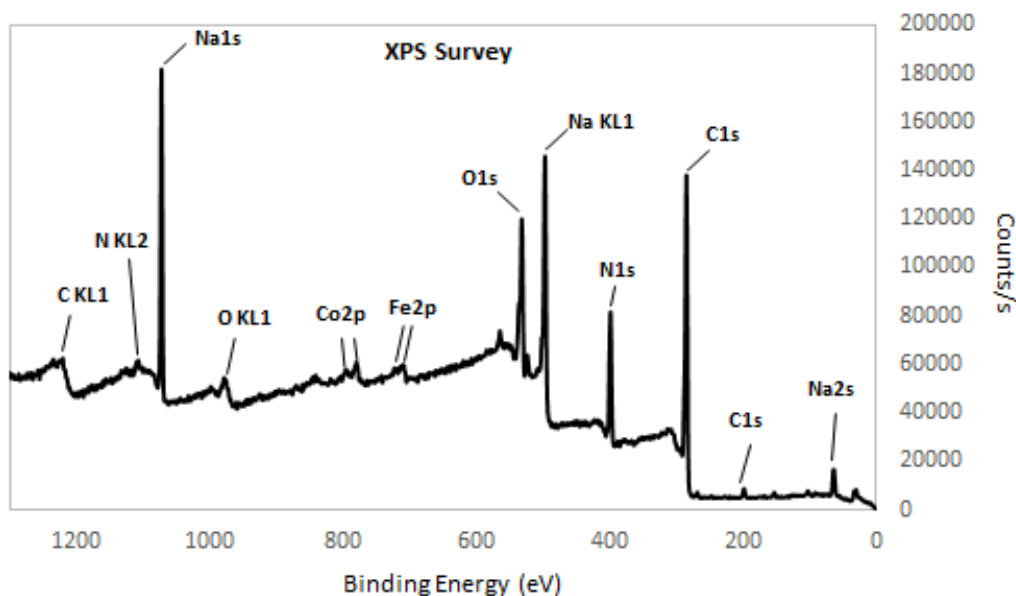


Figure 16. An example XPS survey spectrum of Co^{II}-Fe^{II} PBA LPs formed by the citrate method showing both cobalt and iron peaks. Three spots for each band are analyzed.

2.6.2. Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX) analyses

For SEM analysis, each sample is coated with Au-Pd using Precision Etching Coating System (PECS™). Then, they are transferred to an FEI Quanta 200 FEG instrument for the SEM-EDX analyses. Voltage 20kV and spot size 5 were used for this measurement. The particle sizes were obtained by ImageJ software (Figure 17).

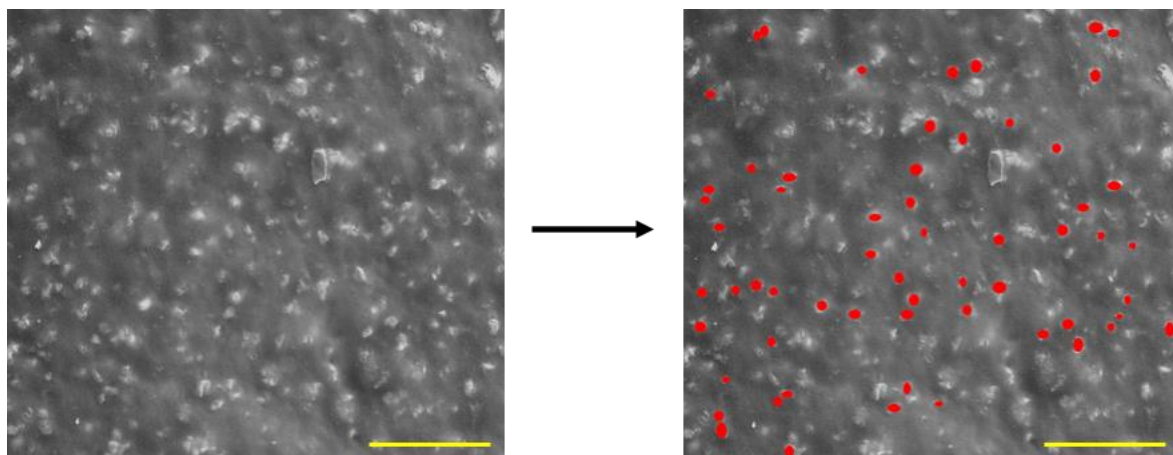


Figure 17. SEM image analysis of Co^{II} - Fe^{II} PBA particles size using ImageJ. Three image spots and around 100 particles in each spot are analyzed for each band. The scale bar represents 30 microns.

Chapter 3

3. Result and Discussion

3.1. Optimization of the Concentrations

The emergence of the PBA Liesegang Patterns is highly concentration-dependent [59]; meaning that the electrolytes' concentrations and the concentration of sodium citrate, polyacrylamide, and the cross-linker must be optimized for the bands to form. Hence, many samples had to be prepared to find the concentrations that provide more bands in a shorter time. I had optimized the diffusing acid solution's solvent and concentration previously (Section 2.3). At this point, I altered the cobalt and iron precursors' concentrations, keeping the concentrations of the other chemicals the same. As shown in Figure 18, five samples of each 97 different concentrations of Co^{2+} and $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, were prepared. Based on the visual observation of A, B, and C (shown on the right of the Figure), I created a 'phase diagram' of the outcome of these 97 concentrations.

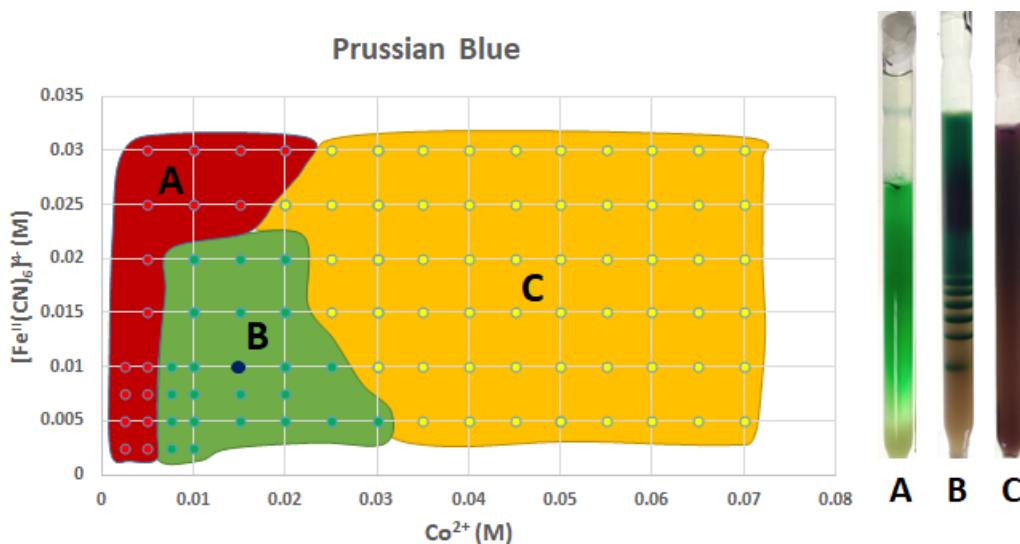


Figure 18. A 'phase diagram' demonstrating the relationship between the concentrations of Co^{2+} and $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ and the type of precipitation under each concentration condition. Region A= continuous precipitation of $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA. Region B = $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA periodic precipitation (LPs) Region C = continuous precipitation. In all the samples, sodium citrate = 0.3 M, HNO_3 = 0.6 M,

acrylamide = 13.5 w%, BIS = 0.056 w%, KPS = 0.187 w%, TEMED = 0.0001 w%, T = 23 °C. *t* = one week (168 h).

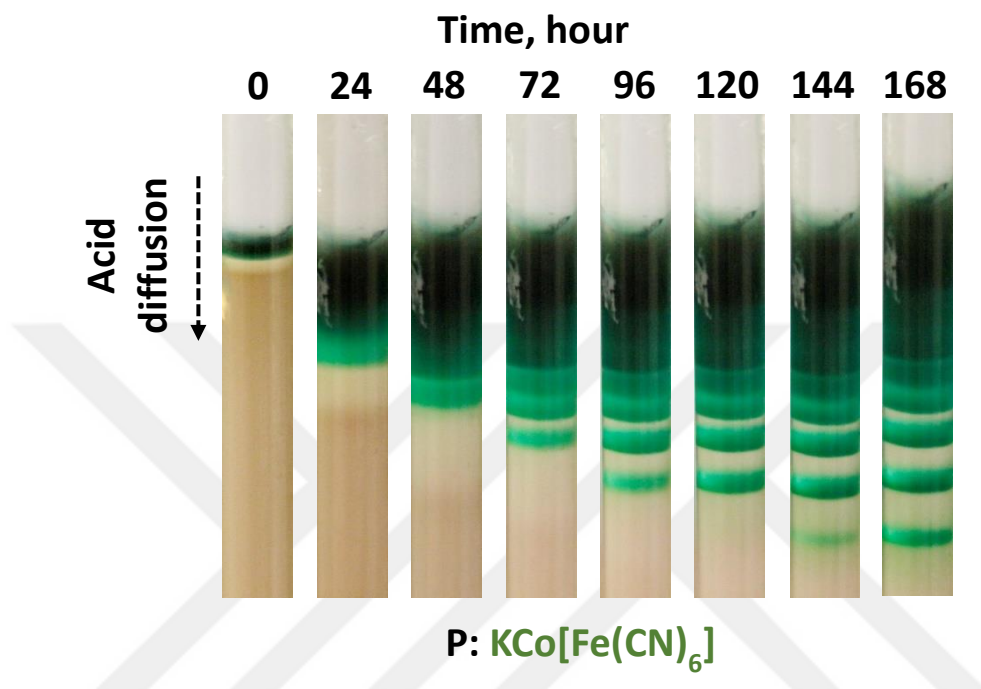


Figure 19. The space-time evolution of cobalt PB Liesegang patterns using citrate-based method resulting in distinct bands after 168 h. $[\text{Co}^{2+}] = 0.015 \text{ M}$, $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-} = 0.010 \text{ M}$, and [sodium citrate] = 0.3 M in the hydrogel is subjected to 0.6 M HNO_3 (in 25% DMF).

According to the phase diagram, when the concentration of cobalt is too low ($\leq 0.005 \text{ M}$) or the concentrations of both electrolytes are high ($\geq 0.025\text{-}0.030 \text{ M}$), continuous precipitation takes place (region A and C). LPs can form only in region B. It should also be noted that the pattern formation is a stochastic event; it is a reaction-diffusion process affected by plenty of factors, meaning that the phase diagram represents the highest possibility of outcomes obtained after repeating the same conditions five times. Among all the points in region B, the one that has the most reproducibility and obedience of the Liesegang bands' empirical laws were chosen for the later experiments (the dark blue point in the diagram). In Figure 19, the spatiotemporal emergence of the $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA LPs using these conditions is shown.

3.1.1. Characterization of 1-D LPs at Room Temperature

The accumulation of small aggregates to form a larger particle is the reason for the formation of LPs. Therefore, to investigate the effect of temperature on the band formation (will be discussed in section 3.2.) and also the catalytic activity of each band (will be discussed in section 3.4.), particles size data is needed. Firstly, the presence and location of the PBA particles in band regions were confirmed by SEM-EDX and XPS. (Figures 20 and 21). The analyses of the particles size were performed using SEM.

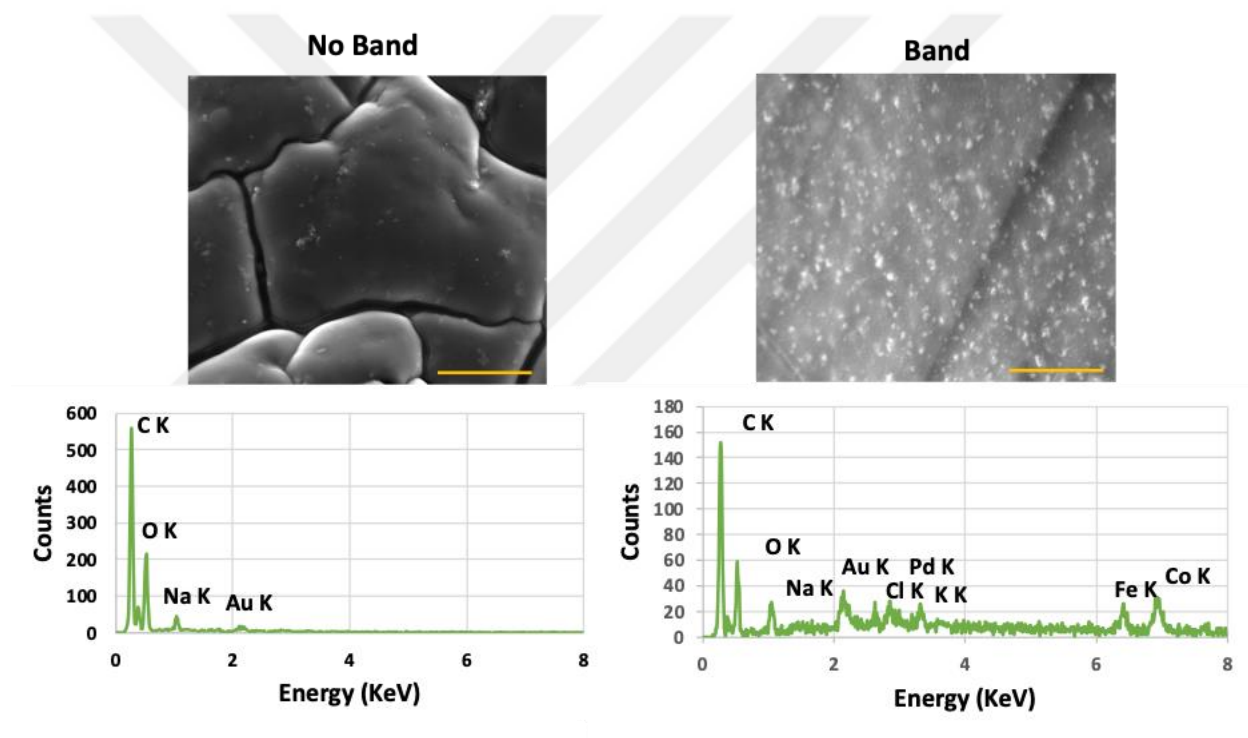


Figure 20. The difference between band region and no-band region in terms of particles shown by SEM images and EDX spectra. The cobalt, iron, potassium, and chlorine peaks are absent in the no-band zone. The scale bar in both images corresponds to 30 microns.

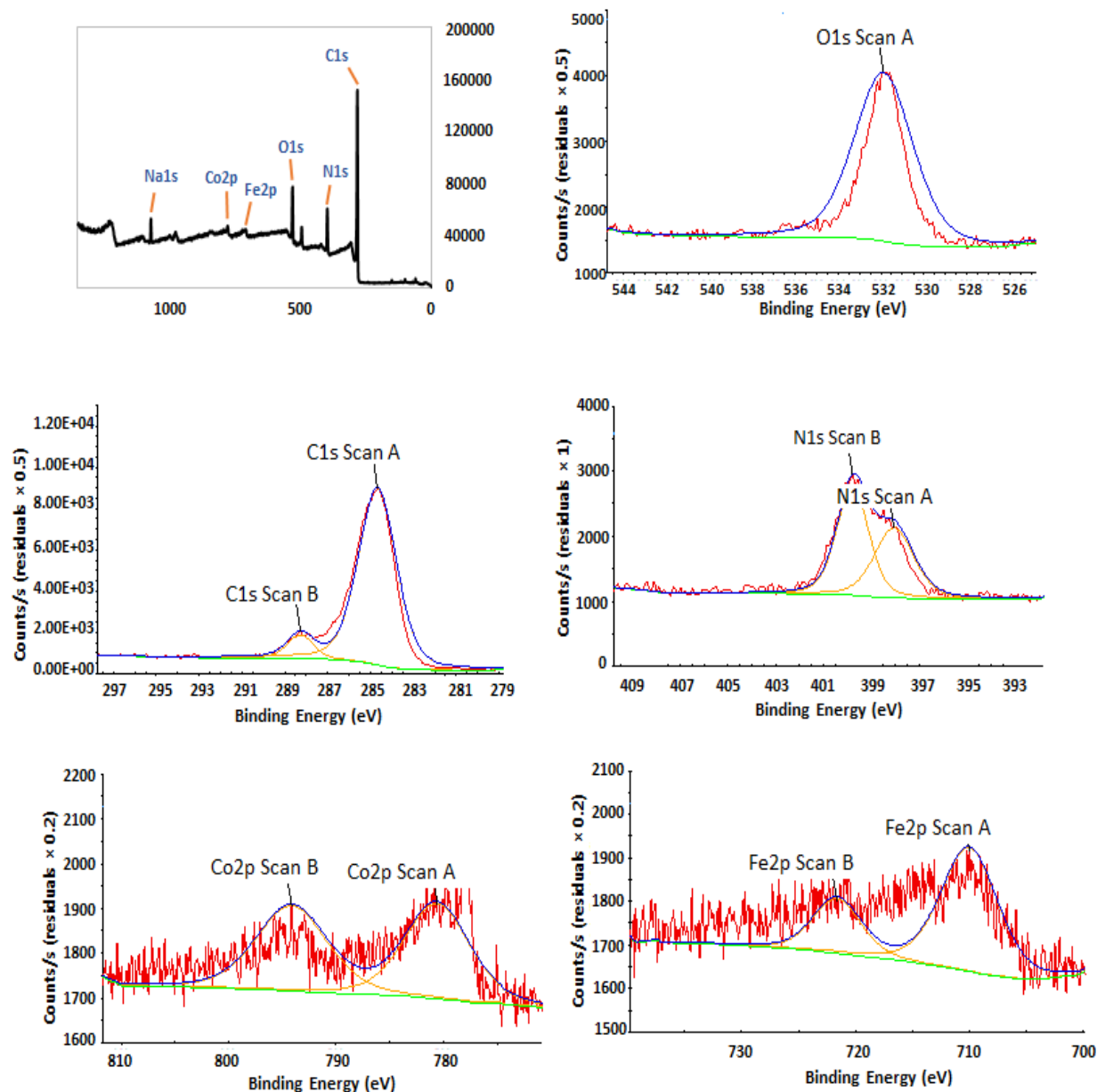


Figure 21. Examples of XPS survey and Hires spectra of $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA LP bands demonstrating cobalt and iron presence in the bands. For the analyzed sample: $[\text{Co}^{2+}] = 0.015 \text{ M}$, $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-} = 0.010 \text{ M}$, and $[\text{sodium citrate}] = 0.3 \text{ M}$ in the hydrogel is subjected to 0.6 M HNO_3 (in 25% DMF). $t=168 \text{ hrs}$.

As seen from the SEM images of the LP band regions (Figure 22), the particles of $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA formed are round-shaped and with sizes in the range of 1-3 microns. In our previous work [66], we have reported that the particles size of the LP product increase as the band number

increases. In the $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA LPs, there is an increase in the particles size with the increase in band number, too. Figure 22 shows the SEM images of each band of the LPs, together with the distributions of particles size. For each sample, in addition to the bands, the continuous precipitation zone (also known as the turbulent zone) was also analyzed.

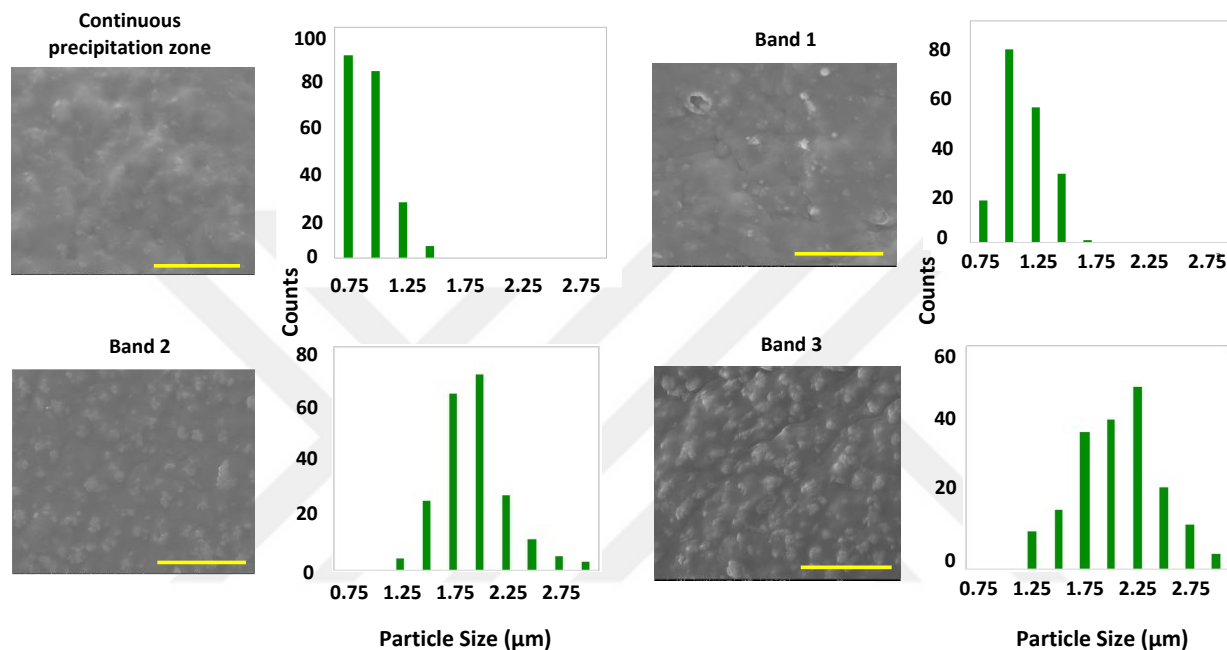


Figure 22. SEM images of $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA Liesegang bands formed at room temperature and the distributions of particle sizes in each band. The average particle sizes increase as the band number increases (farther from the gel/acid interface). The scale bar indicates 30 μm . For the analyzed sample: $[\text{Co}^{2+}] = 0.015 \text{ M}$, $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-} = 0.010 \text{ M}$, and $[\text{sodium citrate}] = 0.3 \text{ M}$ in the hydrogel is subjected to 0.6 M HNO_3 (in 25% DMF). $t=168 \text{ hrs}$.

The increase in particles size with the band number can be attributed to the rate of the reaction front with the inner electrolyte to form the product and the growth rate of the product to form the Prussian blue particle. Based on the time law ($x_n \sim \sqrt{t_n}$), the required time for the pattern formation increases along with the band number, thus resulting in an increase in the particles size in consecutive bands.

Ferrocyanide ($[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$) can be replaced with ferricyanide ($[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$) as the anionic precursor for cobalt PBA LPs preparation. Using the citrate-based method, the bands form in PAM hydrogel after long continuous precipitation but slower than ferrocyanide (they form after 10-14 days). However, this delay in the formation of the LPs has an advantage. The particles in $\text{Co}^{\text{II}}\text{-Fe}^{\text{III}}$ PBA LPs have cubic morphologies with a diameter of around 1 micron (Figure 23). It is known that any change in the precursor for the synthesis of PBA can alter the morphology and, therefore, electronic properties of the material [49]. Despite the interesting features of this product, we did not focus on $\text{Co}^{\text{II}}\text{-Fe}^{\text{III}}$ PBA LPs in this work because PAM cannot be fully gelled in the presence of $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ in the gel, thus making it difficult to cut each band and analyze them.

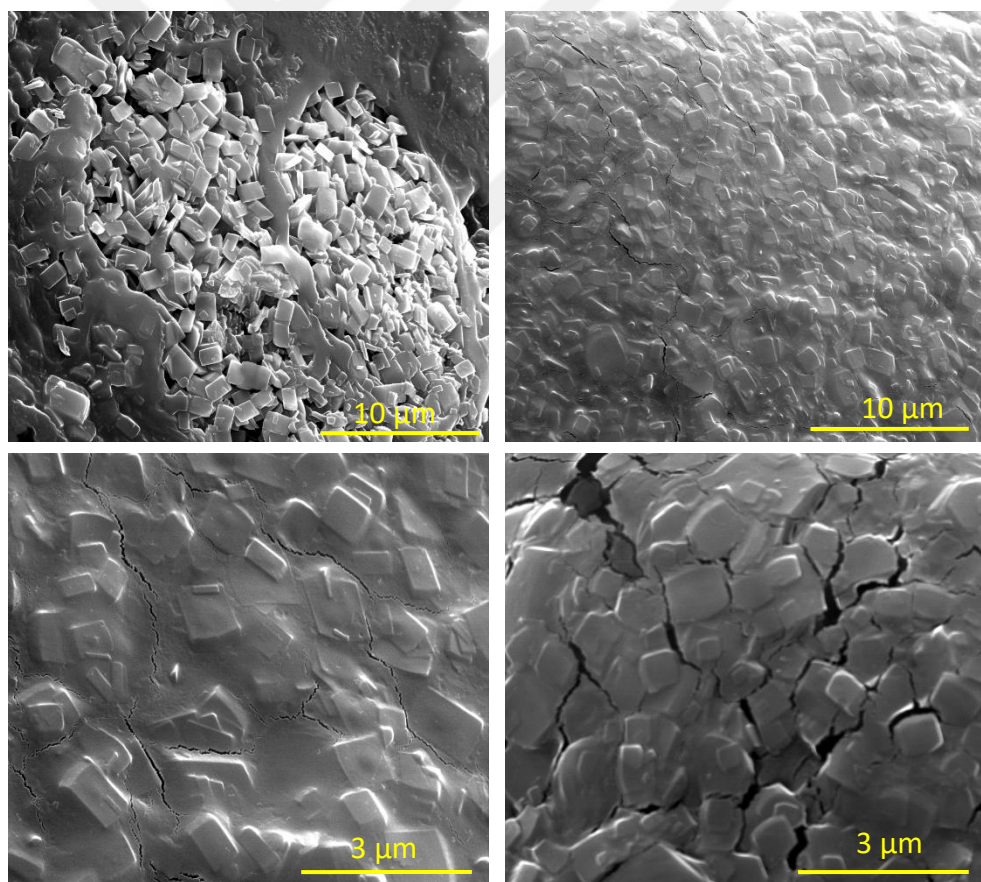


Figure 23. SEM images of the cubic particles of $\text{Co}^{\text{II}}\text{-Fe}^{\text{III}}$ PBA when $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ was used as the anion. For the analyzed samples: $[\text{Co}^{2+}] = 0.015 \text{ M}$, $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-} = 0.010 \text{ M}$, and $[\text{sodium citrate}] = 0.3 \text{ M}$ in the hydrogel is subjected to 0.6 M HNO_3 (in 25% DMF).

3.1.2. Characterization of 2-D LPs at Room Temperature

The diffusion of the acid through the agarose stamp into the hydrogel in two dimensions takes more time, and the reaction is slower than the one-dimensional diffusion. In this case, the particles have more time to grow. Therefore, particle sizes are considerably larger than those obtained in the 1D system. Accordingly, the number of the bands formed usually does not exceed two within the same time of band formation as the 1D case (1 week). In Figure 24, SEM images of the continuous precipitation zone and bands 1 and 2, together with the particle size distributions. In the continuous precipitation region, with the increase in the distance from the stamp contact point, the particles size increase. In the band region, the particles accumulate and form larger clusters.

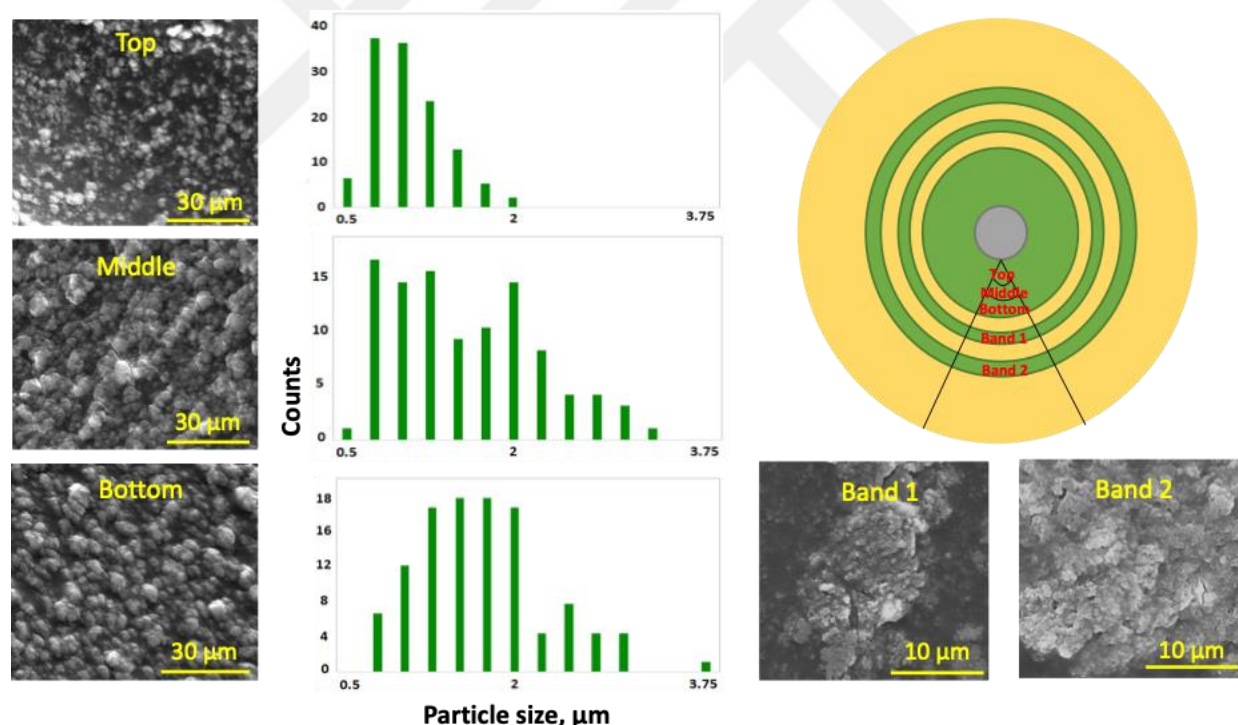


Figure 24. SEM images of 2-D Co^{II}-Fe^{II} PBA Liesegang bands at room temperature and their particle size histograms showing the increase in particles size as the distance from the stamp increases. The particles in the bands aggregate and form clusters. For the analyzed sample: [Co²⁺] = 0.015 M, [Fe^{II}(CN)₆]⁴⁻ = 0.010 M, and [sodium citrate] = 0.3 M in the hydrogel is subjected to 0.6 M HNO₃ (in 25% DMF). t=168 hrs.

3.2. The Temperature Effect

In the formation of Liesegang patterns, the nucleation and growth mechanism, the two electrolytes meet by diffusion of one into the other, they react and initially form an intermediate. This intermediate subsequently transforms into the precipitation product by consuming the local reactants. In conventional LP systems, no other reactions accompany the intermediate's formation and its transformation to the precipitate. In these systems, the temperature affects the diffusion rate, the precipitation threshold (the solubility constant), and the reaction rate. So, the overall effect of temperature on the formation of the LPs can alter according to the chemistry of the system. Despite the complexity of the chemical system, the effect of temperature in the formation of the conventional LPs can be visually tracked and can be quite reproducible. Our previous study shows that the bands' spacing coefficient and the average particles size in bands change with temperature. Vice versa, these macroscopic and microscopic indicators can be controlled by the temperature.

In our approach to form LPs for PBAs through the citrate-based method, we build a more complicated system; acid diffuses to release Co^{2+} ions, bonded to citrate. The temperature affects all the steps; the diffusion rate of the acid, the precipitation threshold, the rates of the reactions of acid with citrate, and the two electrolytes (Co^{2+} and $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$), and finally, the growth of the PB particles. With every 5 °C increase, the spacing coefficient increases (Figure 25b). In this case, we can predict that the temperature increases the precipitation threshold (the solubility product); it takes more time for the electrolyte concentrations to reach the K_{sp} . Therefore, the distance between two adjacent bands increase. In parallel to these, the diffusion coefficient of acid increases, too. The reaction rates should also increase with temperature. However, this effect is less pronounced since the spacing coefficients increase and the bands form at higher distances from the point of contact.

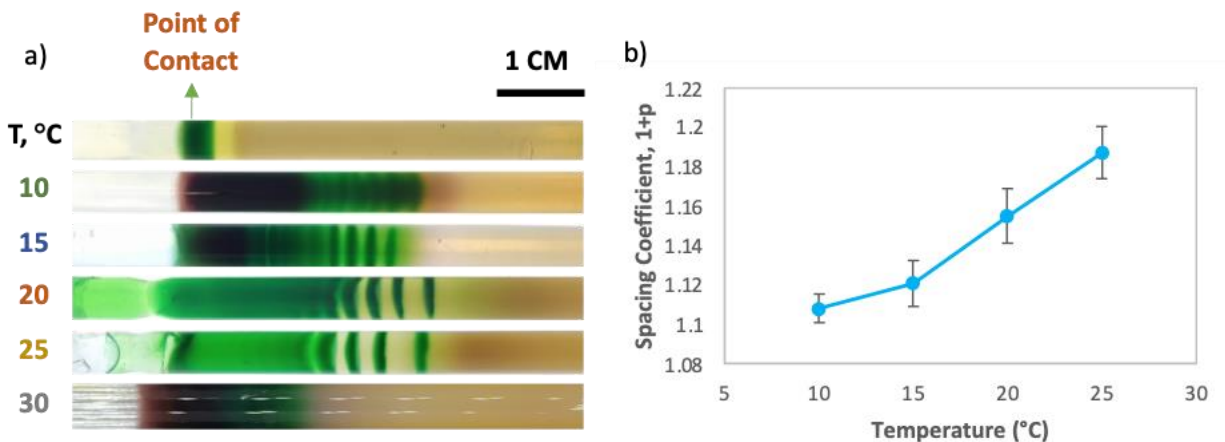


Figure 25. a) The formation of $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA LPs at 10, 15, 20, 25, and 30 °C. The PC represents the point of contact of HNO_3 as the diffusion solution and the PAM hydrogel containing Co^{2+} , $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, and sodium citrate. $[\text{Co}^{2+}] = 0.015 \text{ M}$, $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-} = 0.010 \text{ M}$, and $[\text{sodium citrate}] = 0.3 \text{ M}$ in the hydrogel is subjected to 0.6 M HNO_3 (in 25% DMF). $t = 168 \text{ hrs}$ for all samples. b) The spacing coefficient increases with the increase in temperature. Error bars correspond to standard deviations from at least ten independent experiments.

Another macroscale effect of temperature can be observed in the bending of the bands. Once they form, LP bands are stationary, X_n is a fixed value. However, in our previous work [10], we reported a change in the shape of the bands with the temperature changes – we named it ‘bending’. We attributed this phenomenon to two possibilities in the copper chromate system: inertia or gel deformation. However, in the current study, the temperature is constant throughout the formation of all bands of an LP; therefore, the inertia theory cannot be valid for this system. The other possibility, the gel deformation, can be more pronounced due to acid diffusion, resulting in partial swelling or shrinking of the gel at different temperatures. When the temperature is 10 °C, the bands undergo an outward bending (same direction as the diffusion front), and when the temperature is at 25 °C, the bands undergo an inward bending (Figure 25).

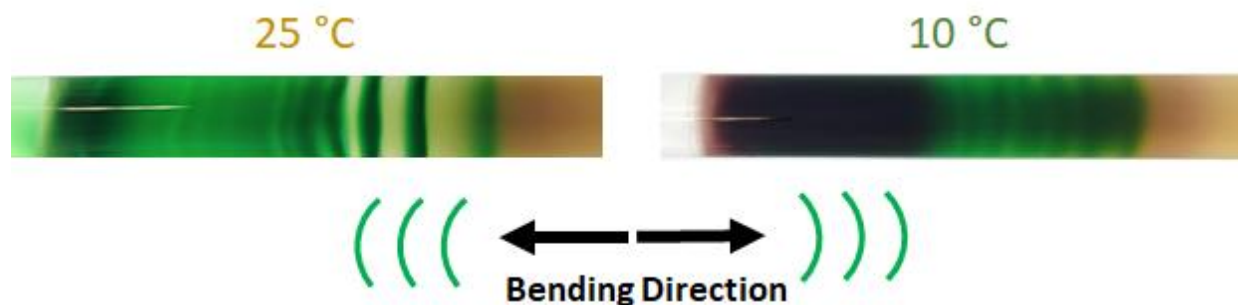


Figure 26. Band bending of Co^{II}-Fe^{II} PBA LPs formed at different temperatures. Outward banding for a low temperature and inward bending for a high temperature. [Co²⁺] = 0.015 M, [Fe^{II}(CN)₆]⁴⁻ = 0.010 M, and [sodium citrate] = 0.3 M in the hydrogel is subjected to 0.6 M HNO₃ (in 25% DMF).

To investigate the effect of temperature on the particles size, the particles of each band of the sample with Co^{II}-Fe^{II} PBA LPs formed at different constant temperatures were analyzed using SEM. In Figure 27a, SEM images are shown together with the histograms of the particles size of the saturated region and the bands 1-3. In contrast to our previous work on the copper chromate system [10] where particles size on the same generation of bands were found to increase with increasing temperature, Co^{II}-Fe^{II} PBA LP systems behave differently toward thermal changes. As shown in Figure 27b, the particles size are generally larger as the band number increases at a constant temperature. However, the particles size behavior is unsystematic within the same band number of the patterns formed at increasing temperatures. This can be attributed to the more complex nature of the system in comparison to the conventional cases, e.g., copper chromate, as we discussed above.

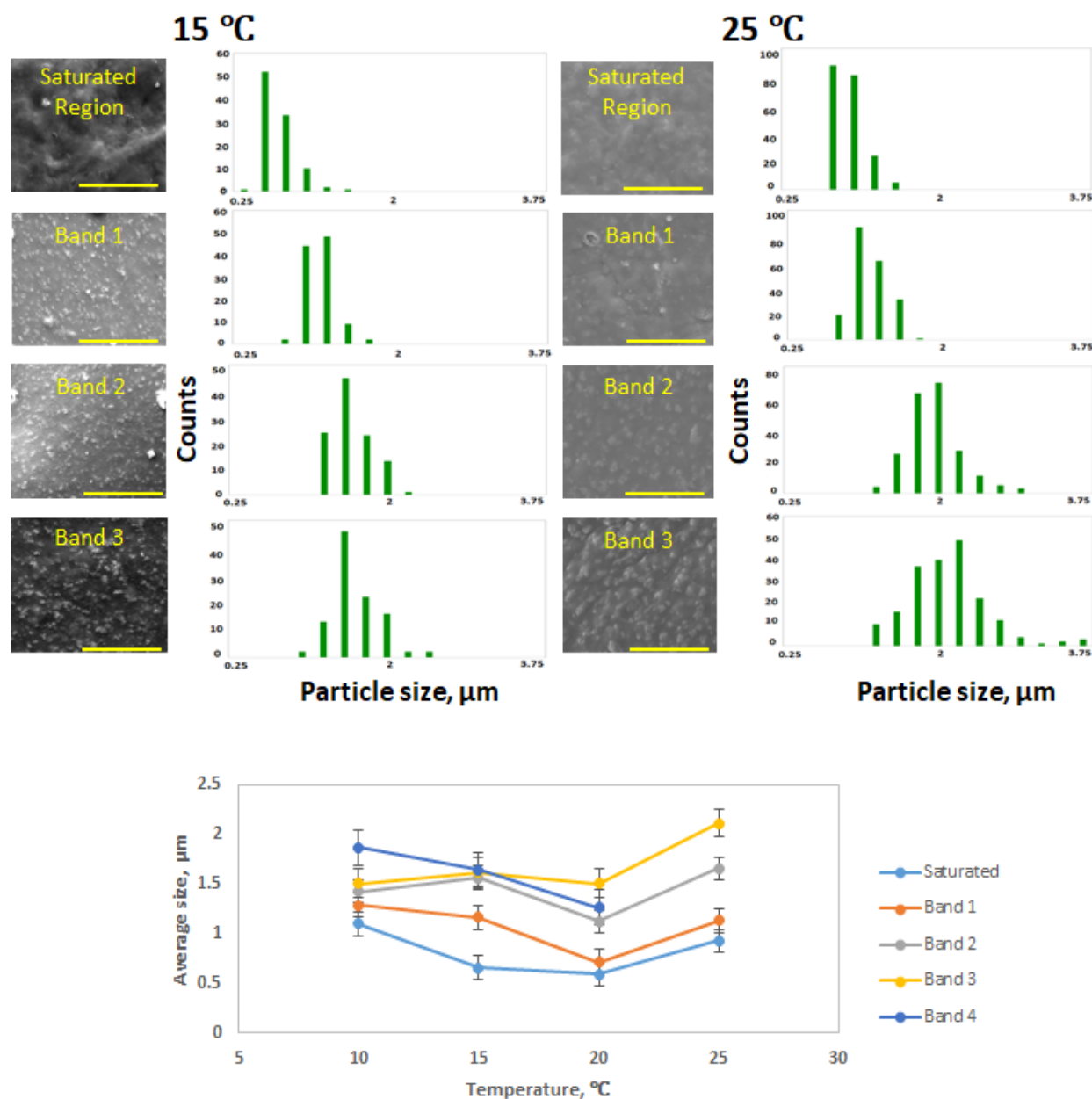


Figure 27. a) SEM images of the saturated region and the bands 1 to 3 of the $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA LPS formed at 15 °C and 25 °C as a comparison to analyze the effect of temperature on the particles size of $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA. In front of the SEM images, histograms with the distributions of particles size are shown. The scale bar indicates 30 μm. b) Average particles size of saturated region and bands 1-5 for the temperature range of 10-25 °C.

3.3. Other PBAs

Due to the different formation rates and the solubility products of PBAs with various metal ions, the pattern formation in each PBA is unique. Since the cation solutions diffuse into the gel in the conventional method for Liesegang pattern formation, the type of gel and its pore size also play a significant role. In addition to cobalt PBA Liesegang patterns, the citrate-based approach can be applied to the Prussian blue and some other Prussian blue analogues. This section discusses the LP formation of $\text{Cu}^{\text{II}}\text{-Fe}^{\text{III}}$ PBA and $\text{Fe}^{\text{III}}\text{-Fe}^{\text{II}}$ PB using this method. Both of these compounds have applications in electrochromism and H_2 storage [67] [68] [69] [70].

3.3.1. Copper PBA

Hayashi et al. showed the copper hexacyanoferrate pattern formation using an electric field with an innovative method called reaction-diffusion-reaction (RDR) [60]. Here, we use the citrate-based method for making the Liesegang pattern of $\text{Cu}^{\text{II}}\text{-Fe}^{\text{III}}$ PBA, where no electric field is needed. Same as in the formation of the $\text{Co}^{\text{II}}\text{-Fe}^{\text{III}}$ PBA, both of the Cu^{2+} (0.010 M) and $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ (0.004 M) ions were dissolved in the polyacrylamide hydrogel containing 0.3 M sodium citrate. After gelation, HNO_3 was added from the top. Figure 28 shows the formation of Liesegang patterns of $\text{Cu}^{\text{II}}\text{-Fe}^{\text{III}}$ PBAs using the citrate-based method and the proposed mechanism responsible for this reaction.

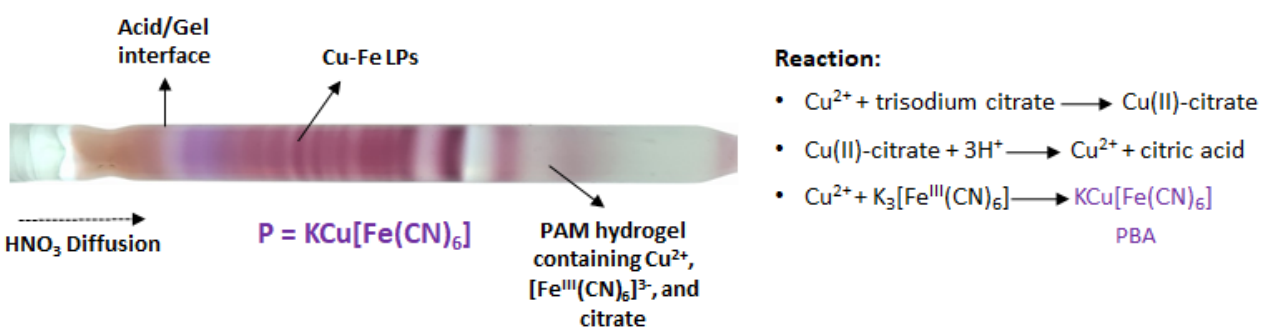


Figure 28. $\text{Cu}^{\text{II}}\text{-Fe}^{\text{III}}$ PBA pattern formation by citrate-based method. Acrylamide = 13.5 w%, BIS = 0.056 w%, KPS = 0.187 w%, TEMED = 0.0005 w%, trisodium citrate = 0.3 M, CuCl_2 = 0.010 M, $\text{K}_3[\text{Fe}^{\text{III}}(\text{CN})_6]$ = 0.004 M, HNO_3 = 0.6 M, $T = 23\text{ }^\circ\text{C}$., $t = 168\text{ h}$.

3.3.2. Fe^{III}-Fe^{II} PB

Although there are studies on the LP formation of PBAs – manganese, cobalt, and copper PBAs – there is yet no study on the iron PB Liesegang patterns. The solubility products of the PBAs mentioned above are in the range of 10^{-13} - 10^{-16} ; however, iron (III) Prussian blue K_{sp} is in the order of 10^{-41} , which makes it quite distinct [71]. Therefore, I prepared a similar system to the other PBAs, in terms of concentrations, but this time with $\text{FeCl}_3 = 0.010 \text{ M}$, $\text{K}_4[\text{Fe}^{\text{II}}(\text{CN})_6] = 0.004 \text{ M}$ in the hydrogel. In my efforts to produce PB LPs, for the first time in the history of Liesegang phenomena, I have observed the reproducible pattern formation in the liquid phase: The periodic precipitation of Fe^{III}-Fe^{II} PB emerged in the acid solution on top of the polyacrylamide hydrogel (and not in the gel!). These PB colloids forming the pattern were stable in the solution for days and did not sediment on the gel/liquid interface (Figure 29). In addition to the bands formed in the acid solution, one or two wide bands also formed in the gel.

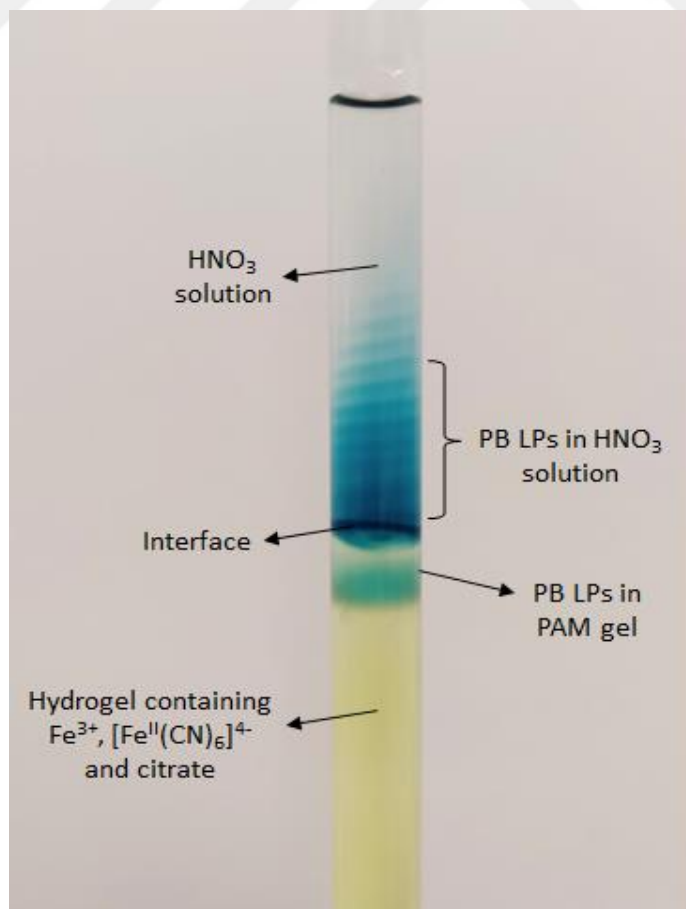


Figure 29. Periodic precipitations of $\text{Fe}^{\text{III}}\text{-Fe}^{\text{II}}$ PB in the acid solution on top of PAM hydrogel using citrate-based method. Acrylamide = 13.5 w%, BIS = 0.056 w%, KPS = 0.187 w%, TEMED = 0.0005 w%, trisodium citrate = 0.3 M, FeCl_3 = 0.010 M, $\text{K}_4[\text{Fe}^{\text{II}}(\text{CN})_6]$ = 0.004 M, HNO_3 = 0.6 M, $T = 23\text{ }^\circ\text{C}$, $t = 72\text{ h}$.

A closer analysis revealed that the hydrogel is swelling after addition of the acid due to osmosis, which causes the mass transport of the formed precipitate on the inner surface of the glass into the solution. Since the solubility product is too low, small colloidal particles are generated that can stay stable in the solution medium compared to large colloids that sediment on the gel/acid interface. A similar band formation also occurred for $\text{In}^{\text{III}}\text{-Fe}^{\text{II}}$ PBA, whose solubility product is around 10^{-44} . In Figure 30, the space-time evolution of the bands can be observed after 1 week. It is necessary to mention that this is just some preliminary hypothesis for this phenomenon, and more experiments are needed for a better discussion.

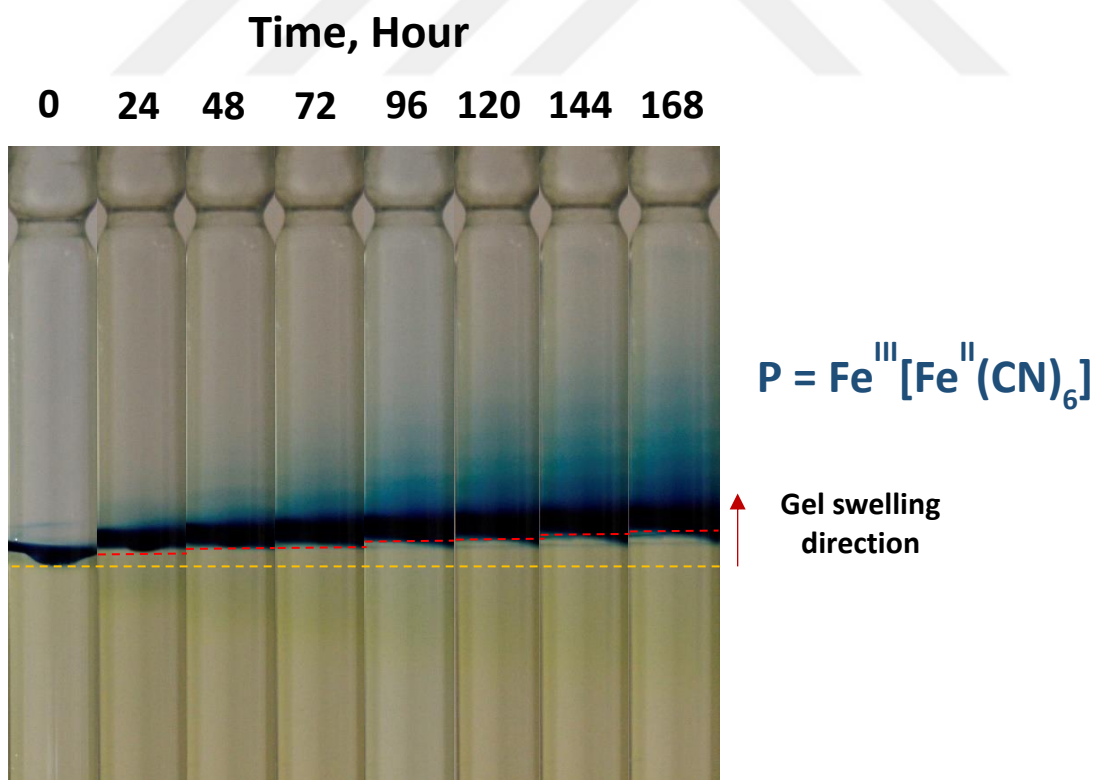


Figure 30. The spatiotemporal evolution of the Prussian blue periodic precipitations in the liquid phase of acid solution due to the periodic swelling of the gel.

3.4. Catalytic Activity

$\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA has shown great potential to be used as a water oxidation catalyst (WOC) by enhancing the rate of the oxygen evolution reaction (OER) [49]. They can function under electrocatalytic (EC) [57], photocatalytic (PC) [72], as well as photoelectrocatalytic (PEC) [73] conditions. For electrocatalysis, a three-electrode system is used. PBA is deposited on FTO-coated glass as the working electrode, a metal cathode (like Pt or Au) works as the counter electrode, and a reference electrode (Ag/AgCl) is utilized to measure the potential. To study PC and PEC water oxidation, the WOC needs to be immersed in the solutions of a photosensitizer (PS) and a semiconductor (SC), respectively, so that by illuminating the light, electrons can be excited from HOMO to LUMO (First, charge transfer from PBA to HOMO of PS or SC, then from HOMO to LUMO by light). PC and PEC are not ideal for our system since the cobalt PBA is inside the gel medium, and the PS or SC diffusion to the PBA is hindered. Therefore, EC water oxidation was selected to investigate the catalytic activity of $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBAs formed.

In the experiments, the gel regions containing each band of the formed LP are cut. These pieces are washed to remove excess PBA reactants and the acid. After washing, the gel pieces are immersed in the solution of 0.5 M KCl for 2 hours to increase the electrical conductivity in the gel media. Then, the gels are placed in the vacuum chamber for two days to dry. To perform the EC water oxidation, we insert the PBA-contained gel (the working electrode) hanging with a wire into a 0.1 M phosphate buffer solution (pH = 7) along with the counter electrode and reference electrode (the wire should not touch the solution). The EC water oxidation setup is shown in Figure 31.



Figure 31. The three-electrode setup for the electrocatalytic water oxidation, in which the cobalt PBA is the working electrode connected to Pt cathode as the counter electrode with an external electric wire, and Ag/AgCl as the reference electrode, all of which immersed in the 0.1 M phosphate buffer solution with pH = 7.

In the experiments, the products formed in the LPs of $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA showed electrocatalytic activity for a water-splitting reaction. However, this activity was not as high as the ones shown with the cobalt hexacyanoferrate powder. This difference can be attributed to the thick gel surrounding the product in the $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA LP bands.

The particles size, the active site surface area, the homogeneity of the particles, and the Co/Fe (active site/inactive site) ratio all affect the catalytic activity of a PBA WOC. Initially, we expected to see a decreasing trend in the catalytic activity of $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA Liesegang bands since the particles are getting larger as we distance from the gel/acid interface (Figure 32). However, we do not see a trend in the catalytic activity from the first band to the last. The main reason for this behavior can be in the preparation of the catalytic samples. Each band is cut manually (a potential error for each cut) and is suspended into the buffer solution with a wire (a significant error since some parts of the gel that has $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA remains outside of the solution so that the wire does not touch the solution); therefore, the amount of the active site in each sample is not precise. Another reason might be the poor diffusion of the reactant in the gel medium, leveling

out all other effects. The determination of the amount of Co^{2+} in the bands was also made through the EDX data, which can bring some uncertainty, too. We should note that we do not see a significant chemical stoichiometry difference between the products forming in each band. We determined the Co/Fe ratio with EDX, the mass of cobalt in the PBA, and the exact chemical formula of the PBA in each band (see Table 2).

Nevertheless, the bands show an increase in current in the region of water oxidation potential (1.23 V) in the cyclic voltammetry (CV), which means the evolution of oxygen. One way to compare the activity of bands and correlate it to the active site is to divide the obtained current at a specific potential to the mass of cobalt in each band. In Figure 32, the cyclic voltammogram of cobalt PBA Liesegang bands in a hydrogel for the same three trials of Table 2 shows the O_2 evolution. Still, due to the reasons mentioned above, no correlation can be made with Table 2. The current data is obtained from the onset potential of the reference electrode (Ag/AgCl), and then as a way to compare and relate them to the active site, they are divided by the mass of cobalt in each band.

		Co:Fe	Mass of Co, mg	Current at 1.2 V, mA/g of Co	onset potential Ag/AgCl, V	Average particle size, μm	Molecular formula
Sample 1	Band 3	1.29	2.71	36.67	1.14	2.40	$\text{K}_{1.42}\text{Co}_{1.29}[\text{Fe}(\text{CN})_6]$
	Band 2	1.33	3.91	19.92	1.16	1.91	$\text{K}_{1.34}\text{Co}_{1.33}[\text{Fe}(\text{CN})_6]$
	Band 1	1.2	2.51	37.29	1.14	1.17	$\text{K}_{1.6}\text{Co}_{1.2}[\text{Fe}(\text{CN})_6]$
	Saturated region	1.21	6.71	12.59	1.17	0.77	$\text{K}_{1.58}\text{Co}_{1.21}[\text{Fe}(\text{CN})_6]$
Sample 2	Band 3	1.36	6.61	17.39	1.16	2.10	$\text{K}_{1.28}\text{Co}_{1.36}[\text{Fe}(\text{CN})_6]$
	Band 2	1.27	4.84	33.67	1.13	2.23	$\text{K}_{1.46}\text{Co}_{1.27}[\text{Fe}(\text{CN})_6]$
	Band 1	1.25	3.1	51.29	1.14	1.33	$\text{K}_{1.5}\text{Co}_{1.25}[\text{Fe}(\text{CN})_6]$
	Saturated region	1.22	21.25	12.09	1.19	1.13	$\text{K}_{1.56}\text{Co}_{1.22}[\text{Fe}(\text{CN})_6]$
Sample 3	Band 3	1.21	7.01	11.74	1.19	2.06	$\text{K}_{1.58}\text{Co}_{1.21}[\text{Fe}(\text{CN})_6]$
	Band 2	1.39	4.68	27.77	1.14	1.96	$\text{K}_{1.22}\text{Co}_{1.39}[\text{Fe}(\text{CN})_6]$
	Band 1	1.37	3.63	21.26	1.16	1.08	$\text{K}_{1.26}\text{Co}_{1.37}[\text{Fe}(\text{CN})_6]$
	Saturated region	1.19	17.48	9.298	1.21	0.92	$\text{K}_{1.62}\text{Co}_{1.19}[\text{Fe}(\text{CN})_6]$

Table 2. Characteristics of each Liesegang band for three samples in terms of particle size, Co/Fe ratio, and the calculated mass of cobalt based on EDX results and the obtained current at a specific potential per gram of cobalt. The current data is obtained based on the onset potential of the reference electrode (Ag/AgCl). The exact PBA molecular formula of each band is determined using the EDX data.

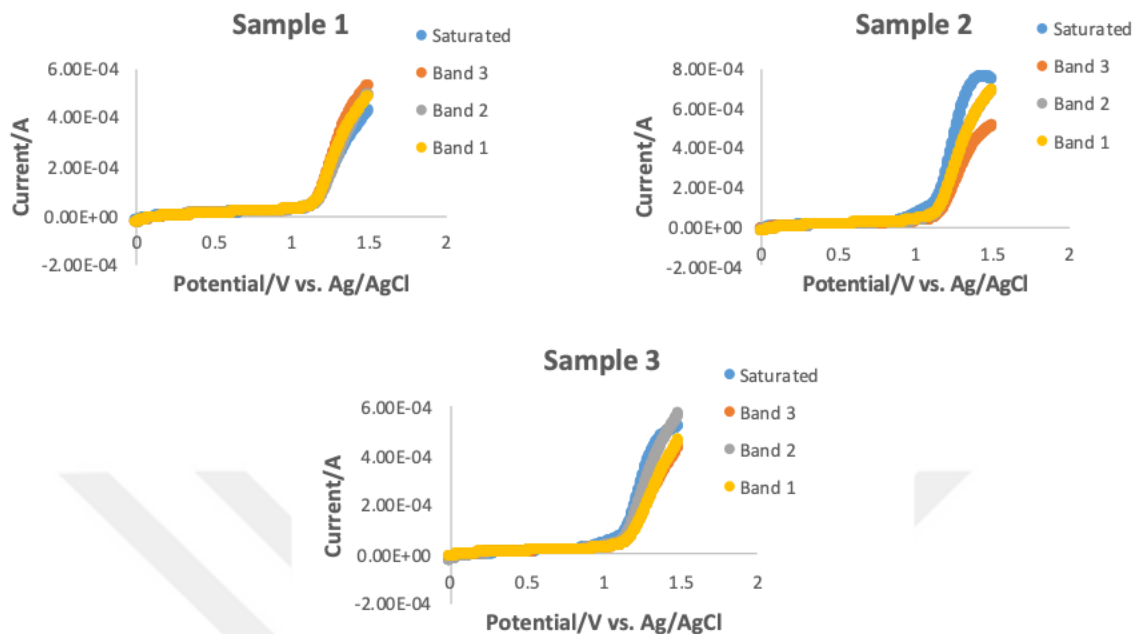


Figure 32. The cyclic voltammograms show the catalytic activity of three bands and the saturated region of $\text{Co}^{\text{II}}\text{-Fe}^{\text{II}}$ PBA LPs for three identically prepared samples. The comparison of the voltammograms and the data acquired and presented in Table 2 shows no correlation between the activity and the band number.

4. Conclusion

This work introduces a new preparation approach for the formation of periodic precipitation patterns for Prussian Blue (PB) and Prussian Blue Analogues (PBAs) based on the reaction-diffusion (RD) system. In this method, the two 'electrolytes' are added into the same medium, with citrate ions that keep the M^{2+} ions from reacting with the ferrocyanide/ferricyanide. The precipitation reaction is initiated by diffusing acid into the medium, which releases the M^{2+} ions to the medium. This way, 1) The precipitation could be obtained as the Liesegang patterns (LP) form, i.e., obeying the mathematical laws of the LP formation, 2) the time to form patterns of a few bands is decreased by order of magnitude, 3) manipulation of the product obtained and precise control over the particles size is attained. The primary focus of this work was on the Co^{II} - Fe^{II} PBA LPs in polyacrylamide hydrogel in 1D and 2D since Co^{II} - Fe^{II} PBA can be used as catalysts in water splitting reactions. In addition to cobalt PBA, LPs formation of Cu^{II} - Fe^{II} PBA and PB using citrate-based method is also studied, both of which led to successful formation of the precipitation patterns. The latter also showed precipitation pattern formation in the acid solution, as an example in the literature.

In this work, the effect of temperature on the LP banding evolution on macroscale and the growth of particles on the microscale were also investigated. Temperature affects a variety of parameters such as the diffusion rate, the reaction rate, the solubility product, and the nature of the gel matrix simultaneously. On the macro scale, this effect could be visually observed and analyzed by mathematical laws to compare the band formation at different temperatures. It was concluded that decreasing the temperature results in decreasing the spacing coefficient. On the microscale, thermal changes affect the particles' size, as shown by SEM measurements. Our study shows the temperature affects the size of particles, but due to the nature of the PBA formation and complexity of our system, we cannot conclude a trend.

In the final part, each Co^{II} - Fe^{II} PBA band in a sample is cut and used as an electrocatalyst for water oxidation reactions using cyclic voltammetry. The bands show an increase in current around the water oxidation potential, which means there is oxygen evolution. However, because of some inevitable experimental errors and the hindered diffusion in the gel medium, no

correlation between the obtained current and the particles size or the amount of the active site (cobalt) could be made.

With this work, I presented a straightforward chemical pathway to the formation of Co^{II} - Fe^{II} PBA LPs. I also showed the advantage of making PBA particles using a reaction-diffusion system: In the LPs, PBAs in each band can have different average particles size, meaning that one can have a set of various products, all in one sample, and forming separately and gradually. I believe that this more practical and reliable experimental procedure, which can also extended be extended to the preparation of PB and PBA LPS, will enable new uses for the patterns. In this work, we tried a sample application of the LP products in catalysis. Since there are many possible applications of using these inorganic networks, I believe combining the applications with the macroscopic and microscopic advantages of LPs can lead to interesting chemical systems and products.

References

- [1] B. A. Grzybowski, *Chemistry in Motion: Reaction-Diffusion Systems for Micro- and Nanotechnology*. 2009.
- [2] S. Sadek and R. Sultan, *Liesegang patterns in nature : A diverse scenery across the sciences*, vol. 661, no. July 2016. 2010.
- [3] H. Nabika, "Liesegang Phenomena: Spontaneous Pattern Formation Engineered by Chemical Reactions," *Curr. Phys. Chem.*, vol. 5, no. 1, pp. 5–20, 2015, doi: 10.2174/187794680501150908110839.
- [4] Z. Rácz, "Formation of Liesegang patterns," *Phys. A Stat. Mech. its Appl.*, vol. 274, no. 1, pp. 50–59, 1999, doi: 10.1016/S0378-4371(99)00432-X.
- [5] S. Thomas, G. Varghese, and I. Lagzi, "The width of Liesegang bands: A study using moving boundary model and simulation," *Pramana - J. Phys.*, vol. 78, no. 1, pp. 135–145, 2012, doi: 10.1007/s12043-011-0204-2.
- [6] S. N. Swami, and K. Kant, "Liesegang Rings of Copper Chromate in Gelatin Gel Rings of copper chromate in these media , it," vol. 110, no. 1904, pp. 3–4, 1958.
- [7] A. Packter, "Inverted Rhythmic Precipitation," *Nature*, vol. 176, p. 1955, 1955.
- [8] N. Kanniah, F. D. Gnanam, P. Ramasamy, and G. S. Laddha, "Revert and direct type Liesegang phenomenon of silver iodide," *J. Colloid Interface Sci.*, vol. 80, no. 2, pp. 369–376, 1981, doi: 10.1016/0021-9797(81)90195-8.
- [9] T. Karam, H. El-Rassy, and R. Sultan, "Mechanism of revert spacing in a PbCrO₄ Liesegang system," *J. Phys. Chem. A*, vol. 115, no. 14, pp. 2994–2998, 2011, doi: 10.1021/jp200619g.
- [10] M. Turab, A. Khan, J. K. Yiğitbaşı, P. Tootoonchian, M. Morsali, I. Lagzi, B. Baytekin, *ACS Appl. Mater. Interfaces*, pp. 1–7, 2022, doi: 10.1021/acsami.1c20640.
- [11] H. K. Henisch, "Liesegang ring formation in gels," *J. Cryst. Growth*, vol. 76, no. 2, pp. 279–289, 1986, doi: 10.1016/0022-0248(86)90372-6.
- [12] E. Ramírez-Álvarez *et al.*, "On the dynamics of Liesegang-type pattern formation in a gaseous system," *Sci. Rep.*, vol. 6, no. August 2015, pp. 1–13, 2016, doi: 10.1038/srep23402.
- [13] J. A. Pask and C. W. Parmelee, "Study of Diffuison In Glass," *J. Am. Ceram. Soc.*, vol. 26, no.

- 8, pp. 267–277, 1943.
- [14] I. T. Bensemann, M. Fialkowski, and B. A. Grzybowski, “Wet stamping of microscale periodic precipitation patterns,” *J. Phys. Chem. B*, vol. 109, no. 7, pp. 2774–2778, 2005, doi: 10.1021/jp047885b.
 - [15] S. K. Smoukov, I. Lagzi, and B. A. Grzybowski, “Independence of primary and secondary structures in periodic precipitation patterns,” *J. Phys. Chem. Lett.*, vol. 2, no. 4, pp. 345–349, 2011, doi: 10.1021/jz101679t.
 - [16] I. Ferenc and I. Lagzi, “Models of Liesegang pattern formation,” vol. 661, no. 2, p. 10, 2010, [Online]. Available: <http://eprints.eemcs.utwente.nl/17384/>.
 - [17] D. A. Smith, “On Ostwald’s supersaturation theory of rhythmic precipitation (Liesegang’s rings),” *J. Chem. Phys.*, vol. 81, no. 7, pp. 3102–3115, 1984, doi: 10.1063/1.448012.
 - [18] G. T. Dee, “Patterns Produced by Precipitation at a Moving Reaction Front,” vol. 5, no. July, pp. 5–8, 1986.
 - [19] R. Feeney, S. L. Schmidt, P. Strickholm, J. Chadam, and P. Ortoleva, “Periodic precipitation and coarsening waves: Applications of the competitive particle growth model,” *J. Chem. Phys.*, vol. 78, no. 3, pp. 1293–1311, 1983, doi: 10.1063/1.444867.
 - [20] Z. Rácz, “Formation of Liesegang Patterns: A Spinodal Decomposition Scenario,” *Phys. A Stat. Mech. its Appl.*, vol. 274, no. 1, pp. 50–59, 1999, doi: 10.1016/S0378-4371(99)00432-X.
 - [21] R. Matalon and A. Packter, “The Liesegang phenomenon. I. Sol protection and diffusion,” pp. 46–62, 1954.
 - [22] M. Saad, A. Safieddine, and R. Sultan, “Revisited Chaos in a Diffusion-Precipitation-Redissolution Liesegang System,” *J. Phys. Chem. A*, vol. 122, no. 29, pp. 6043–6047, 2018, doi: 10.1021/acs.jpca.8b03229.
 - [23] H. Zhang *et al.*, “Three dimension Liesegang rings of calcium hydrophosphate in gelatin,” *J. Sol-Gel Sci. Technol.*, vol. 71, no. 3, pp. 597–605, 2014, doi: 10.1007/s10971-014-3411-8.
 - [24] E. C. H. Davies, “Liesegang rings. I. Silver chromate in gelatin and colloidal gold in silicic acid gel,” *J. Am. Chem. Soc.*, vol. 44, no. 12, pp. 2698–2704, 1922, doi: 10.1021/ja01433a003.

- [25] I. Lagzi, "Formation of Liesegang patterns in an electric field," *Phys. Chem. Chem. Phys.*, vol. 4, no. 8, pp. 1268–1270, 2002, doi: 10.1039/b109835g.
- [26] H. Hayashi, S. Aoki, and H. Abe, "Magnetic-Field-Induced Painting-Out of Precipitation Bands of Mn-Fe-Based Prussian Blue Analogues in Water-Glass Gels," *ACS Omega*, vol. 3, no. 4, pp. 4494–4501, 2018, doi: 10.1021/acsomega.8b00285.
- [27] M. Morsali *et al.*, "Mechanical Control of Periodic Precipitation in Stretchable Gels to Retrieve Information on Elastic Deformation and for the Complex Patterning of Matter," *Adv. Mater.*, vol. 32, no. 10, pp. 1–7, 2020, doi: 10.1002/adma.201905779.
- [28] J. M. García-Ruiz, D. Rondón, A. García-Romero, and F. Otálora, "Role of gravity in the formation of liesegang patterns," *J. Phys. Chem.*, vol. 100, no. 21, pp. 8854–8860, 1996, doi: 10.1021/jp953351m.
- [29] A. Arango-Restrepo, D. Barragán, and J. M. Rubi, "Nonequilibrium self-assembly induced Liesegang rings in a non-isothermal system," *Phys. Chem. Chem. Phys.*, vol. 20, no. 7, pp. 4699–4707, 2018, doi: 10.1039/c7cp08469b.
- [30] T. Isemura, "Studies on Rhythmic Precipitates," *Bull. Chem. Soc. Jpn.*, vol. 14, no. 6, pp. 179–237, 1939, doi: 10.1246/bcsj.14.179.
- [31] I. Neamtu *et al.*, "Characterization of poly (acrylamide) as temperature- sensitive hydrogel," vol. 8, no. 5, pp. 1939–1943, 2006.
- [32] R. Atmani, M. E. L. Kouali, M. Talbi, and A. E. L. Brouzi, "Study of the Effect of Temperature on Diffusion of a Liquid of Simulation inside the Polyethylene Vinyl Acetate," *Int. J. Adv. Chem. Eng. Biol. Sci.*, vol. 3, no. 1, pp. 81–84, 2016, doi: 10.15242/ijacebs.ae0416117.
- [33] Y. Matos-Peralta and M. Antuch, "Review—Prussian Blue and Its Analogs as Appealing Materials for Electrochemical Sensing and Biosensing," *J. Electrochem. Soc.*, vol. 167, no. 3, p. 037510, 2020, doi: 10.1149/2.0102003jes.
- [34] A. Ludi, "Prussian blue, an inorganic evergreen," *J. Chem. Educ.*, vol. 58, no. 12, p. 1013, 1981, doi: 10.1021/ed058p1013.
- [35] M. Ware, "Prussian blue: Artists' pigment and chemists' sponge," *J. Chem. Educ.*, vol. 85, no. 5, 2008, doi: 10.1021/ed085p612.
- [36] P. Day, N. S. Hush, and R. J. H. Clark, "Mixed valence: Origins and developments," *Philos.*

- Trans. R. Soc. A Math. Phys. Eng. Sci.*, vol. 366, no. 1862, pp. 5–14, 2008, doi: 10.1098/rsta.2007.2135.
- [37] G. C. Allen and N. S. Hush, “Intervalence-Transfer Absorption. Part 1. Qualitative Evidence for Intervalence-Transfer Absorption in Inorganic Systems in Solution and in the Solid State,” vol. 8, pp. 357–389, 2007, doi: 10.1002/9780470166093.ch6.
- [38] L. I. Doumic, G. Salierno, C. Ramos, P. M. Haure, M. C. Cassanello, and M. A. Ayude, “‘Soluble’: Vs. ‘insoluble’ Prussian blue based catalysts: Influence on Fenton-type treatment,” *RSC Adv.*, vol. 6, no. 52, pp. 46625–46633, 2016, doi: 10.1039/c6ra06618f.
- [39] V. V. Pavlishchuk, I. A. Koval, E. Goresnik, A. W. Addison, G. A. Van Albada, and J. Reedijk, “The first example of a true ‘Turnbull’s Blue’ family compound with trapped iron oxidation states,” *Eur. J. Inorg. Chem.*, no. 1, pp. 297–301, 2001, doi: 10.1002/1099-0682(20011)2001:1<297::AID-EJIC297>3.0.CO;2-N.
- [40] W. J. Li, C. Han, G. Cheng, S. L. Chou, H. K. Liu, and S. X. Dou, “Chemical Properties, Structural Properties, and Energy Storage Applications of Prussian Blue Analogues,” *Small*, vol. 15, no. 32, pp. 1–21, 2019, doi: 10.1002/sml.201900470.
- [41] A. A. Karyakin, “Prussian blue and its analogues: Electrochemistry and analytical applications,” *Electroanalysis*, vol. 13, no. 10, pp. 813–819, 2001, doi: 10.1002/1521-4109(200106)13:10<813::AID-ELAN813>3.0.CO;2-Z.
- [42] H. Yi *et al.*, “Structure and Properties of Prussian Blue Analogues in Energy Storage and Conversion Applications,” *Adv. Funct. Mater.*, vol. 31, no. 6, pp. 1–25, 2021, doi: 10.1002/adfm.202006970.
- [43] S. Qiu, Y. Xu, X. Wu, and X. Ji, “Prussian Blue Analogues as Electrodes for Aqueous Monovalent Ion Batteries,” *Electrochem. Energy Rev.*, no. 0123456789, 2021, doi: 10.1007/s41918-020-00088-x.
- [44] A. A. Karyakin, O. V. Gitelmacher, and E. E. Karyakina, “A high-sensitive glucose amperometric biosensor based on prussian blue modified electrodes,” *Anal. Lett.*, vol. 27, no. 15, pp. 2861–2869, 1994, doi: 10.1080/00032719408000297.
- [45] T. Yamamoto, Y. Umemura, M. Nakagawa, T. Iyoda, and Y. Einaga, “Photochromism induced magnetization changes in Prussian Blue ultrathin films fabricated into the

- Langmuir-Blodgett films composed of an amphiphilic azobenzene and a deoxyribonucleic acid,” *Thin Solid Films*, vol. 515, no. 13, pp. 5476–5483, 2007, doi: 10.1016/j.tsf.2007.01.019.
- [46] T. C. Liao, W. H. Chen, H. Y. Liao, and L. C. Chen, “Multicolor electrochromic thin films and devices based on the Prussian blue family nanoparticles,” *Sol. Energy Mater. Sol. Cells*, vol. 145, pp. 26–34, 2016, doi: 10.1016/j.solmat.2015.08.004.
- [47] L. Hedley, L. Porteous, D. Hutson, N. Robertson, and J. O. Johansson, “Electrochromic bilayers of Prussian blue and its Cr analogue,” *J. Mater. Chem. C*, vol. 6, no. 3, pp. 512–517, 2018, doi: 10.1039/c7tc04521b.
- [48] R. J. Kulesza, M. A. Malik, K. Miecznikowski, and A. Wolkiewicz, “Counteraction - Sensitive Electrochromism of Cobalt Hexacyanoferrate Films Counteraction-Sensitive Electrochromism of Cobalt Hexacyanoferrate Films,” pp. 10–13, 1996.
- [49] T. G. Ulusoy Ghobadi, E. Ozbay, and F. Karadas, “How to Build Prussian Blue Based Water Oxidation Catalytic Assemblies: Common Trends and Strategies,” *Chem. - A Eur. J.*, vol. 27, no. 11, pp. 3638–3649, 2021, doi: 10.1002/chem.202004091.
- [50] P. Xiong, G. Zeng, L. Zeng, and M. Wei, “Prussian blue analogues $\text{Mn}[\text{Fe}(\text{CN})_6]0.6667 \cdot n\text{H}_2\text{O}$ cubes as an anode material for lithium-ion batteries,” *Dalt. Trans.*, vol. 44, no. 38, pp. 16746–16751, 2015, doi: 10.1039/c5dt03030g.
- [51] S. Wheeler, I. Capone, S. Day, C. Tang, and M. Pasta, “Low-Potential Prussian Blue Analogues for Sodium-Ion Batteries: Manganese Hexacyanochromate,” *Chem. Mater.*, vol. 31, no. 7, pp. 2619–2626, 2019, doi: 10.1021/acs.chemmater.9b00471.
- [52] Z. Jia, J. Wang, and Y. Wang, “Electrochemical sodium storage of copper hexacyanoferrate with a well-defined open framework for sodium ion batteries,” *RSC Adv.*, vol. 4, no. 43, pp. 22768–22774, 2014, doi: 10.1039/c4ra02559h.
- [53] S. Mukherjee, B. R. Rao, B. Sreedhar, P. Paik, and C. R. Patra, “Copper Prussian blue analogue: Investigation into multifunctional activities for biomedical applications,” *Chem. Commun.*, vol. 51, no. 34, pp. 7325–7328, 2015, doi: 10.1039/c5cc00362h.
- [54] X. Zhang *et al.*, “In-situ integration of nickel-iron Prussian blue analog heterostructure on Ni foam by chemical corrosion and partial conversion for oxygen evolution reaction,”

- Electrochim. Acta*, vol. 363, p. 137211, 2020, doi: 10.1016/j.electacta.2020.137211.
- [55] W. J. A. S. Gomes, C. De Oliveira, and F. Huguenin, “Energy Harvesting by Nickel Prussian Blue Analogue Electrode in Neutralization and Mixing Entropy Batteries,” *Langmuir*, vol. 31, no. 31, pp. 8710–8717, 2015, doi: 10.1021/acs.langmuir.5b01419.
- [56] E. Eren and A. Uygün Oksuz, “Flexible nickel Prussian blue analogue films for electrochromic and H₂O₂ sensing,” *J. Mater. Sci. Mater. Electron.*, vol. 31, no. 18, pp. 15434–15445, 2020, doi: 10.1007/s10854-020-04106-y.
- [57] S. Pintado, S. Goberna-Ferrón, E. C. Escudero-Adán, and J. R. Galán-Mascarós, “Fast and persistent electrocatalytic water oxidation by Co-Fe Prussian blue coordination polymers,” *J. Am. Chem. Soc.*, vol. 135, no. 36, pp. 13270–13273, 2013, doi: 10.1021/ja406242y.
- [58] H. Hayashi, S. Aoki, and T. Suzuki, “Spontaneous precipitation pattern formation by crystallites of Mn-Fe-based Prussian blue analogues in agarose gel,” *RSC Adv.*, vol. 9, no. 62, pp. 36240–36247, 2019, doi: 10.1039/c9ra07960b.
- [59] H. Hayashi, Y. Sato, and H. Abe, “X-ray spectroscopic analysis of stochastic, periodic precipitation in Co-Fe-Based Prussian blue analogues,” *J. Anal. At. Spectrom.*, vol. 33, no. 6, pp. 957–966, 2018, doi: 10.1039/c8ja00068a.
- [60] H. Hayashi and T. Suzuki, “A reaction-diffusion-reaction system for forming periodic precipitation bands of cu-fe-based prussian blue analogues,” *Appl. Sci.*, vol. 11, no. 11, 2021, doi: 10.3390/app11115000.
- [61] H. Hayashi, Y. Sato, S. Aoki, and M. Takaishi, “In situ XRF analysis of Cs adsorption by the precipitation bands of Prussian blue analogues formed in agarose gels,” *J. Anal. At. Spectrom.*, vol. 34, no. 5, pp. 979–985, 2019, doi: 10.1039/c9ja00025a.
- [62] H. Zhu, H. Li, H. Song, and S. Liao, “Effect of sodium citrate on preparation of nano-sized cobalt particles by organic colloidal process,” *Front. Chem. China*, vol. 4, no. 2, pp. 154–159, 2009, doi: 10.1007/s11458-009-0022-y.
- [63] W. Wang *et al.*, “Reversible structural evolution of sodium-rich rhombohedral Prussian blue for sodium-ion batteries,” *Nat. Commun.*, vol. 11, no. 1, pp. 1–9, 2020, doi: 10.1038/s41467-020-14444-4.
- [64] H. Yan, Y. Zhao, C. Qiu, and H. Wu, “Micropatterning of inorganic precipitations in

- hydrogels with soft lithography,” *Sensors Actuators, B Chem.*, vol. 132, no. 1, pp. 20–25, 2008, doi: 10.1016/j.snb.2008.01.002.
- [65] Y. Shimizu, J. Matsui, K. Unoura, and H. Nabika, “Liesegang Mechanism with a Gradual Phase Transition,” *J. Phys. Chem. B*, vol. 121, no. 11, pp. 2495–2501, 2017, doi: 10.1021/acs.jpcc.7b01275.
- [66] R. M. Walliser *et al.*, “Growth of nanoparticles and microparticles by controlled reaction-diffusion processes,” *Langmuir*, vol. 31, no. 5, pp. 1828–1834, 2015, doi: 10.1021/la504123k.
- [67] L. Reguera, C. P. Krap, J. Balmaseda, and E. Reguera, “Hydrogen storage in copper prussian blue analogues: Evidence of H₂ coordination to the copper atom,” *J. Phys. Chem. C*, vol. 112, no. 40, pp. 15893–15899, 2008, doi: 10.1021/jp803714j.
- [68] A. P. Baioni, M. Vidotti, P. A. Fiorito, E. A. Ponzio, and S. I. C. De Torresi, “Synthesis and characterization of copper hexacyanoferrate nanoparticles for building up long-term stability electrochromic electrodes,” *Langmuir*, vol. 23, no. 12, pp. 6796–6800, 2007, doi: 10.1021/la070161h.
- [69] L. M. N. Assis, R. Leones, J. Kanicki, A. Pawlicka, and M. M. Silva, “Prussian blue for electrochromic devices,” *JEAC*, vol. 777, pp. 33–39, 2016, doi: 10.1016/j.jelechem.2016.05.007.
- [70] C. P. Krap, J. Balmaseda, B. Zamora, and E. Reguera, “Hydrogen storage in the iron series of porous Prussian blue analogues,” *Int. J. Hydrogen Energy*, vol. 35, no. 19, pp. 10381–10386, 2010, doi: 10.1016/j.ijhydene.2010.07.109.
- [71] J. A. Dean, *LANGE’S HANDBOOK OF CHEMISTRY*, vol. 10, no. 6. 2015.
- [72] S. Goberna-Ferrón, W. Y. Hernández, B. Rodríguez-García, and J. R. Galán-Mascarós, “Light-driven water oxidation with metal hexacyanometallate heterogeneous catalysts,” *ACS Catalysis*, vol. 4, no. 6, pp. 1637–1641, 2014, doi: 10.1021/cs500298e.
- [73] F. S. Hegner, I. Herraiz-Cardona, D. Cardenas-Morcoso, N. López, J. R. Galán-Mascarós, and S. Gimenez, “Cobalt Hexacyanoferrate on BiVO₄ Photoanodes for Robust Water Splitting,” *ACS Appl. Mater. Interfaces*, vol. 9, no. 43, pp. 37671–37681, 2017, doi: 10.1021/acsami.7b09449.

