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Interplay between synthesis conditions, crystal structure, morphology and OER activity of $AgFeO_2$ delafossite materials

$AgFeO_2$ delafosit malzemelerin sentez koşulları, kristal yapısı, morfolojisi ve OER aktivitesi arasındaki ilişki

Yazar (lar) (Author(s)): *Doğan ÇİRMİ[1], Özkan GÖRMEZ[2], Barış SAÇLI[3], Uğur ÇAĞLAYAN[4], Muharrem KUNDURACI[5]*

ORCID[1]: 0000-0002-5608-398X

ORCID[2]: 0000-0002-1360-9275

ORCID[3]: 0000-0003-1386-7490

ORCID[4]: 0000-0001-7646-1119

ORCID[5]: 0000-0003-0670-5987

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Highlights

- *Increasing temperature and NaOH mass favor 3R polytype in $AgFeO_2$ delafossite material*
- *In the temperature and NaOH mass ranges studied, 2H and 3R type samples were always nm and µm sized, respectively.*
- *2H type delafossites showed better OER activity*

Graphical Abstract

In this study, delafossite type $AgFeO_2$ materials were synthesized by hydrothermal method and their OER activity were tested by Linear Scan Voltammetry method.

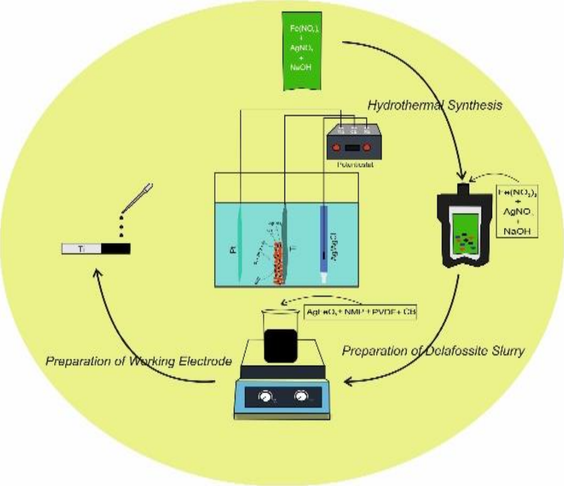

Figure. Electrochemical testing and hydrothermal synthesis of AgFeO2 delafossite materials

Aim

The aim of this work is to find a correlation between crystal structure and oxygen evolution activity of delafossite type $AgFeO_2$ material

Design & Methodology

By altering hydrothermal synthesis conditions, $AgFeO_2$ delafossites with varying degrees of 3R and 2H phases were prepared. Materials were characterized with XRD, SEM and XPS techniques. The oxygen evolution activity of different samples was analyzed using Linear Scan Voltammetry method.

Originality

A comparison of 2H-$AgFeO_2$ and 3R-$AgFeO_2$ delafossites in terms of their oxygen evolution activity is conducted for the first time in literature.

Findings

It was determined that temperature and NaOH mass played a significant role in the crystal structure of $AgFeO_2$ delafossite material. Increasing synthesis temperature and NaOH quantity favor 3R phase at the expense of 2H phase. Delafossites with a mixture of 2H-$AgFeO_2$ and 3R-$AgFeO_2$ phases exhibited better oxygen evolution current than single-phase 3R-$AgFeO_2$ delafossites.

Conclusion

According to the test results, it was determined that the synthesis conditions played a significant change in the phase structure of delafossite $AgFeO_2$ and different phase structures affected the electrocatalytic activity.

Declaration of Ethical Standards

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permissionDğ

Interplay Between Synthesis Conditions, Crystal Structure, Morphology and OER Activity of $AgFeO_2$ Delafossite Materials

Araştırma Makalesi / Research Article

Doğan ÇİRMİ[1*], Özkan GÖRMEZ[1], Barış SAÇLI[1], Uğur ÇAĞLAYAN[2], Muharrem KUNDURACI[3]

[1]Mersin University, Faculty of Science and Letters, Deparment of Chemistry, Mersin /Turkey
[2]Çukurova University, Central Research Laboratory, Adana/Turkey
[3]Tarsus University, Faculty of Aeronautics and Astronautics, Deparment of Aerospace Engineering, Mersin/Turkey

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ABSTRACT

In this current study, delafossite type $AgFeO_2$ materials were synthesized using the hydrothermal method. Depending on synthesis temperature (115, 155 or 180 ^{o}C) and NaOH mineralizer mass (1.0, 1.6, 2.0 or 2.4 g) amount, the delafossites were composed of either mixed-phase 3R/2H-$AgFeO_2$ or single-phase 3R-$AgFeO_2$ crystals. Higher temperatures and NaOH mass were helpful to the growth of µm-sized 3R (space group of R-3m) crystals while lower temperatures and mineralizer mass produced nm-sized 2H (space group of P63/mmc) crystals. The comparison of different delafossite samples revealed that the oxygen evolution reaction (OER) current was larger in mixed-phase materials. Also, the transition from two-phase system to single-phase system was accompanied with a sudden drop in OER current. On the other hand, the difference between the electrochemical behavior of 3R and 2H phase delafossite is discussed in detail by considering similar studies in the literature.

Keywords: $AgFeO_2$, delafossite, hydrothermal method, oxygen evolution reaction .

$AgFeO_2$ Delafosit Malzemelerin Sentez Koşulları, Kristal Yapısı, Morfolojisi ve OER Aktivitesi Arasındaki İlişki

ÖZ

Bu çalışmada, delafosit yapılı $AgFeO_2$ malzemeleri hidrotermal yöntem kullanılarak sentezlenmiştir. Sentez sıcaklığına (115, 155 veya 180 ^{o}C) ve NaOH miktarına (1,0, 1,6, 2,0 veya 2,4 g) bağlı olarak delafosit malzemeler ya çift-fazlı 3R/2H-$AgFeO_2$ ya da tek-fazlı 3R-$AgFeO_2$ kristallerden oluşmuştur. Yüksek sıcaklıklar ve NaOH miktarındaki artış µm boyutlu 3R (uzay grubu R-3m) kristallerin büyümesine yardımcı olurken, düşük sıcaklık ve NaOH miktarındaki azalış nm boyutlu 2H (uzay grubu P63/mmc) kristallerin oluşumunu desteklemiştir. Farklı delafosit malzemelerin kıyaslaması sonucu, oksijen çıkış tepkimesi akımının çift-fazlı malzemelerde daha yüksek olduğu belirlenmiştir. Ayrıca, çift-fazlı sistemden tek-fazlı sisteme geçişte oksijen çıkış tepkimesi akımında ani düşüş görülmüştür. Elde edilen veriler ışığında, 3R ve 2H fazlı delafositlerin elektrokimyasal davranışları arasındaki fark, literatürdeki benzer çalışmalar da dikkate alınarak ayrıntılı olarak tartışılmıştır.

Anahtar Kelimeler: $AgFeO_2$, delafosit, hidrotermal yöntem, oksijen çıkış reaksiyonu

1. INTRODUCTION

Electrochemical water splitting is a sustainable and environmentally friendly technological process that involves the production of hydrogen and oxygen gases. The electrolysis of water includes the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). OER is a more demanding reaction that requires the occurrence of multiple steps such as multi-electron transfers, O–H bond breaking and O–O bond formation [1]. In order to overcome these challenging steps, it is necessary to develop effective electrocatalysts. It is known that noble metal oxides such as IrO_2 and RuO_2 exhibit high catalytic activity for OER [2-3]. However, the high cost and rarity of these catalysts create a disadvantage in industrial applications. For this reason, extensive research studies have been carried out to develop high activity and low-cost electrocatalysts instead of noble metal catalysts. Many of these have reported that transition metal oxides with perovskite [4-5], spinel [6-7] or delafossite [8-9] type crystal structures can show good OER activity.

Delafossite materials are a group of materials with the general formula of $A^{+1}B^{+3}O_2$. Two polytypes are observed depending on the stacking of layers; 3R with space group of R-3m and 2H with space group of P63/mmc [10-11]. Their electronic conductivity can

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*Sorumlu yazar(Corresponding Author)
e-posta : dogancirmi@mersin.edu.tr

range from metallic to semiconductors depending on the use of A and B atoms [12]. Owing to this ability, the delafossites have recently started to receive attention in energy conversion applications as electro-catalyst or photo-catalyst [13-15]. Different delafossites such as $CuCoO_2$, $CuScO_2$, $AgFeO_2$ were demonstrated to exhibit good electrochemical activity in KOH electrolyte [9,16-17]. However, to our best knowledge, there is no report that links phase structure (3R vs. 2H) and morphology to OER activity in delafossite materials.

In this work, we chose $AgFeO_2$ for its easy synthesis and nontoxicity and prepared several materials under different conditions using the hydrothermal technique. Temperature and NaOH mass played a significant role in the space group and particle size of prepared materials. Delafossites with 2H type consisted of nanosized particles and exhibited better oxygen evolution activity than their µm-sized 3R counterparts.

2. MATERIAL AND METHOD

2.1. Synthesis of $AgFeO_2$ via Hydrothermal Technique

The synthesis of $AgFeO_2$ delafossite was carried out by modifying the method used by Moghaddam et al. [15]. In the experiments, a custom-made stainless steel reactor with Teflon chamber was used for hydrothermal synthesis of $AgFeO_2$ samples. A 10 mL solution containing 1.61 g $Fe(NO_3)_3.9H_2O$ and 0.68 g $AgNO_3$ was initially prepared inside teflon chamber and mixed for 10 minutes. Then, a separate 20 mL NaOH solution prepared at different concentrations was added to the previous mixture at 20 drops/min. The final solution was mixed with a magnetic stirrer at 400 rpm for 15 min. After the lid of the steel reactor was tightly closed, the air in the reactor was purged several times with nitrogen gas. The reactor was placed onto the heating plate and heated to a predetermined value (115-180 °C). The pressure inside the reactor was brought to 40 atm by injecting nitrogen gas. After spending 5 hr at this temperature, the steel reactor was cooled to room temperature with the help of a water bath. Finally, the obtained solid was washed several times with distilled water and dried at 60°C for 24 hours.

2.2. Physical Characterization of $AgFeO_2$

The crystal structures $AgFeO_2$ materials were analyzed by a PANalytical Empyrean X-ray diffractometer using CuKα radiation. The diffraction patterns were collected between 2θ=10º and 70º at a scan rate of 2º min^{-1}. The FIA-Quanta FEG 650 model scanning electron microscope (SEM) was used to study the particle morphology of delafossite powders. The oxidation states of Ag and Fe atoms in $AgFeO_2$ were determined by an X-ray photoelectron spectrometer (XPS, PHI 5000 VersaProbe). The peak positions were calibrated by referencing the C1s peak position at 284.8 eV and shifting other peaks in the spectrum accordingly.

2.3. Preparation of Titanium Supported $AgFeO_2$

In order to prepare the OER electrode, a slurry containing 200 mg of $AgFeO_2$ active material, 25 mg of carbon black as a conductive agent, 25 mg of polyvinylidenedifluoride (PVDF) binder and 2 g of N-methyl-2-pyrrolidinone (NMP) solvent was prepared. About 20-30 mg of this slurry was initially cast onto a titanium electrode (1 cm^2) and later dried at 150 ºC for 10 min to remove NMP solvent. The same procedure was followed for all nine samples and the mass loading of active material was 2-3 mg in each electrode.

2.4. Electrochemical Studies

The electrochemical studies were carried out by linear sweep voltammetry (LSV) using a CHI 660A electrochemical workstation. A three electrode cell with Ti supported $AgFeO_2$ as working electrode, Pt foil as counter electrode and $Ag/AgCl/KCl_{sat}$ as reference electrode was used for all measurements. The OER activity of $AgFeO_2$ samples was evaluated in 0.5 M KOH electrolyte using LSV between 0-1.2 V (vs. Ag/AgCl) at a scan rate of 10 mV/s. Each LSV scan was carried out twice for repeatability. The potentials displayed in graphs were obtained by converting the measured potentials from the reference electrode to the reversible hydrogen electrode (RHE) using the formula E(RHE)=E(Ag/AgCl) + 0.197 + 0.059pH.

3. RESULTS AND DISCUSSION

The X-ray diffraction patterns of $AgFeO_2$ samples were prepared at different temperature and the mass of NaOH are plotted in Fig 1. All of the peaks were assigned to 3R-$AgFeO_2$ (JCPDS:75-2147) or 2H-$AgFeO_2$ (JCPDS:25-0765) phases [18-19]. The absence of any secondary peaks belonging to Ag_2O or Fe_2O_3 proves the success of synthesis to produce single material. Although, the two phases have many overlapping peaks, 34-36º range can be used for qualitative analysis as distinct peaks can be noticed within this region, namely (101) and (012) peaks of 3R-$AgFeO_2$ at 34.4º and 35.4º, respectively and (101) peak of 2H-$AgFeO_2$ at 34.9º. A detailed look at patterns reveals that phase formation shows a strong dependence on temperature and NaOH mass. It is noticed that higher temperature and NaOH mass favor 3R-$AgFeO_2$ phase at the expense of its 2H counterpart. However, the fact that the dominant phase is 2H-$AgFeO_2$ in all 115 ºC samples regardless of NaOH mass or in all 1 gr NaOH samples regardless of temperature indicates that both parameters need to be high enough to obtain 3R-$AgFeO_2$ type single phase material.

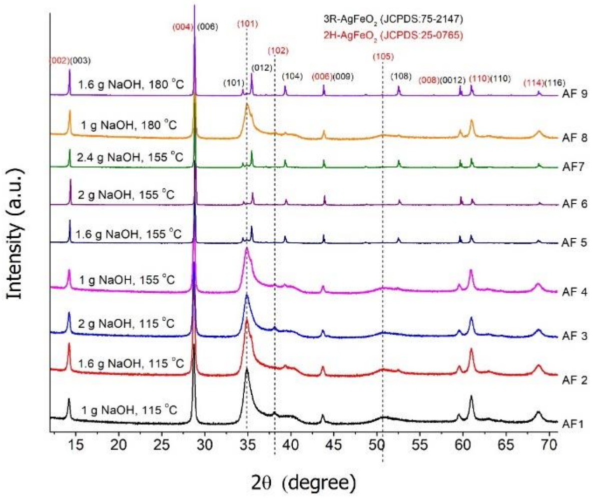

Figure 1. X-ray diffraction patterns of different AgFeO$_2$ samples

In order to obtain quantitative results, the Rietveld refinement was carried out on all samples to calculate the percentages of 3R and 2H phases. The experimental and simulated patterns of AF3 are given in Fig. 2 as an example. The percentage of the 3R-AgFeO$_2$ phase was found to be about 30-40% in AF1, AF2, AF3, AF4 and AF8 while it was over 95% in other samples. The accuracy of calculations was lowered by the presence of too many overlapping peaks from both phases.

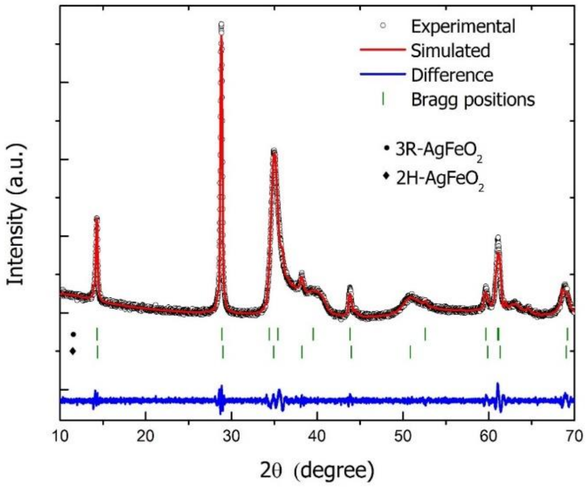

Figure 2. Rietveld refinement for the X-ray diffraction pattern of AF3 sample

The preferential growth of 3R phase with increasing NaOH mass was reported previously for CuFeO$_2$ delafossite [20], and our results are in agreement with this study. Since both crystal structures are very similar to each other, an explanation for the underlying reason behind such phenomena is absent in the literature. However, it is speculated that improved solubility of metal reagents inside water enabled by NaOH mineralizer favors the growth of R-3m crystals. The fact that higher synthesis temperatures are also conducive to this phase supports the solubility hypothesis.

The morphological properties of AgFeO$_2$ samples were examined by scanning electron microscopy (SEM) and the images of six samples are given in Fig. 3. The primary particle size in AF4 is close to 50 nm and the size distribution seems to be quite uniform. However, a small number of disk-shaped secondary structures with 200-300 nm in size are also noticed. Since 2H-AgFeO$_2$ crystals are the dominant phase in all 3 samples, these larger secondary particles could belong to 3R-AgFeO$_2$. All these observations were valid for similarly nanostructured AF1, AF2 and AF3 delafossites as well.

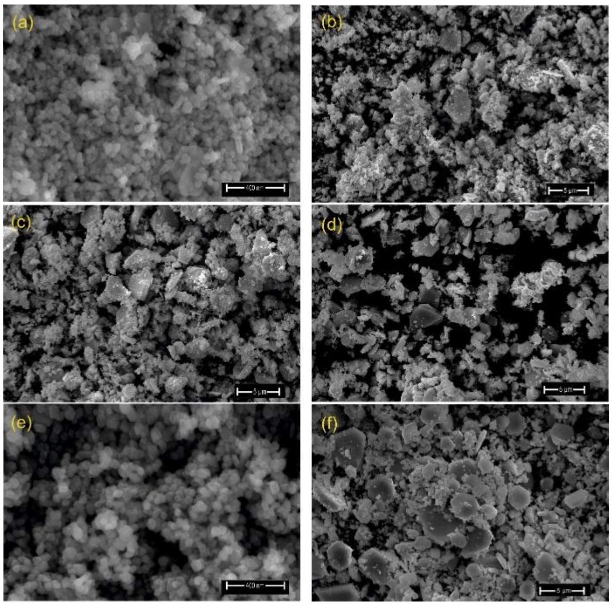

Figure 3. SEM images of different AgFeO$_2$ samples. a) AF4 b) AF5 c) AF6 d) AF7 e) AF8 f) AF9. The scale bar is 400 nm for AF4 and AF8 and 5 μm for the others

A quite drastic change in particle size was observed with switch from 2H-AgFeO$_2$ dominant AF4 to 3R-AgFeO$_2$ dominant AF5, AF6 and AF7. A slight increase of NaOH mass from 1 g to 1.6 g in the synthesis was enough to transform nano-sized primary particles into several μm-sized aggregates. These irregular aggregates seem to be composed of sub-μm primary particles. With the further addition of mineralizer into the reactor, aggregates get even larger reaching up to 5 μm in diameter and their surfaces appear flatter and more faceted. It can be concluded that increasing NaOH mass helps growth kinetics of 3R-AgFeO$_2$ delafossite material. Finally, as for 180 ºC samples, the same behavior was observed. Specifically, when NaOH mass was limited to 1 g, AgFeO$_2$ delafossite is made of 2H-richer nanoparticles. Upon increasing the mineralizer mass to 1.6 g, 2H phase almost disappeared and particle morphology changed to large and faceted form. Based on X-ray diffraction and scanning electron microscopy results, some conclusions can be drawn. The 2H-AgFeO$_2$ phase has a higher nucleation rate than 3R-AgFeO$_2$ and forms first. But, when ionic mobilities of Ag and Fe elements in solution are enhanced via rising temperature and mineralizer content, 3R-$AgFeO_2$ becomes the more favorable phase as its growth rate is faster. These mechanisms explain the observation of nm-sized 2H-$AgFeO_2$ and μm-sized 3R-$AgFeO_2$.

In order to further characterize the delafossite samples, X-ray photoelectron spectroscopy measurements were performed to determine the oxidation states of Ag and Fe elements for AF4. The results are shown in Fig. 4. In Fig 4a, the peaks at 368.6 eV and 374.6 eV correspond to $3d_{5/2}$ and $3d_{3/2}$ of Ag^+, respectively [21]. As for the XPS spectrum of iron in Fig. 4b, the Fe 2p has two main peaks, $2p_{3/2}$ peak at 725.4 eV and $2p_{1/2}$ peak at 711.8.0 eV. These binding energies correspond to Fe^{+3} [22].

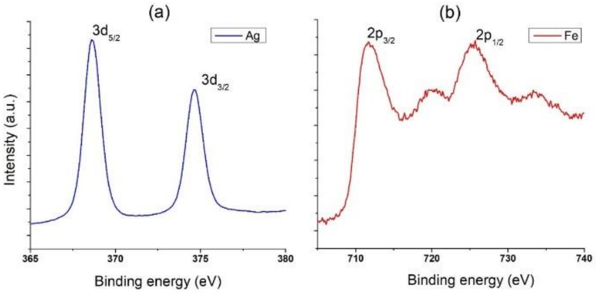

Figure 4. X-ray photoelectron spectroscopy patterns of $AgFeO_2$ delafossite material

A summary of the synthesis conditions, crystal structures, morphological characteristics together with OER activity data of nine $AgFeO_2$ materials are given in Table 1. It is noticed that the oxygen evolution activity is better with 3R/2H-$AgFeO_2$ mixed-phase delafossites than 3R-$AgFeO_2$ only delafossites. For example, the delafossites AF1, AF2, AF3 and AF4 have similar phase mixture and particle sizes. Their oxygen evolution current at -2.2 V vs. RHE has an average value of about 17.5 A/g. On the other hand, with the addition of extra NaOH in the synthesis, 3R-$AgFeO_2$ becomes the overwhelming phase and the current value suddenly drops to 15.4 and 11 A/g with AF5 and AF6 electrodes, respectively. A similar scenario is observed with AF8 and AF9 samples as well. Namely, mixed 3R/2H-$AgFeO_2$ AF8 reaches an OER current of 13.8 A/g as opposed to 8.8 A/g with 3R-$AgFeO_2$ only AF9.

The linear scan voltammetry profiles of a few select $AgFeO_2$ electrodes are plotted in Fig.5. The onset potential for oxygen evolution is around 1.6 V vs. RHE for all samples. This value is in close proximity with other delafossite materials [22-24]. However, as oxygen gas evolution speeds up with increasing oxidation potential values, the distinction between mixed 3R/2H-$AgFeO_2$ and 3R-$AgFeO_2$ electrodes becomes much more visible in favor of mixed-phase delafossite.

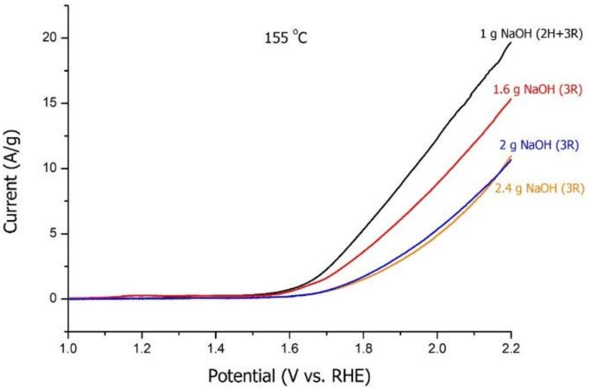

Figure 5. Anodic linear voltammetry scan of $AgFeO_2$ electrodes prepared using varying amounts of NaOH mass

It should be pointed out that the transition from two-phase 3R/2H delafossite to 3R-only delafossite is also accompanied by a significant change in particle size and shape. While the 3R/2H-$AgFeO_2$ materials are composed of distinct nanoparticles under 100 nm in diameter, the particles in 3R-$AgFeO_2$ materials are in the range of 1-5 μm. So, a reasonable question arises as to the origin of electrochemical activity between 2H-$AgFeO_2$ and 3R-$AgFeO_2$ delafossites. A part of this difference can be attributed to the appreciable particle size difference between both materials. As the catalytic activity in any material is highly dependent on the overall surface area, the poorer performance of 3R-$AgFeO_2$ can originate from its large number of μm-sized particles. This effect can be most easily observed among 3R-$AgFeO_2$ only AF5, AF6, AF7 and AF9 materials. Since all these materials have the same phase structure, the differences in OER activity are solely from the particle size effect. Since higher temperature and NaOH mass favor particle growth, it is not surprising that AF9 delafossite (180 ^{o}C and 1.6 g NaOH) with the largest primary particles exhibits the smallest oxygen evolution current.

If we compare 2H-$AgFeO_2$ and 3R-$AgFeO_2$ delafossites from a more fundamental perspective, there are a very limited number of publications that studied this issue. Miclau et. al. [25] compared 2H and 3R $CuAlO_2$ for DSSC activity and reported that the presence of small amount of 2H phase significantly improved the performance. The better performance was attributed to the higher electronic conductivity of 2H-$CuAlO_2$. However, the measured bandgap difference was only 0.03 eV, thereby raising doubt about their argument. Toyoda et. al. [12] studied the degree of e_g and t_{2g} occupancy as an OER activity descriptor for several copper delafossites, and their DFT calculations showed a very slight advantage in favor of 3R delafossites. Based on these results, it appears that there is no significant difference between 2H and 3R delafossites in terms of electronic conductivity and band gap structure. Pumera et. al. [26] reported that 3R-MoS_2 displayed better HER activity than 2H-MoS_2 but offered no explanation. On the other hand, Ma et. al. [17] studied the role of crystal structure on the activation of peroxymonosulfate and found out that 2H-$AgFeO_2$ has a more conducive surface layer than 3R-$AgFeO_2$ in terms of binding to OH- radicals and works better as a catalyst. Their measurements were also supported by DFT calculations. Since oxygen evolution reaction also relies on the attachment of hydroxyl groups on the catalyst surface, their results are relevant here and can be used to validate the 2H vs 3R activity difference in our measurements.

Table 1. Summary of synthesis conditions, space group, particle size and OER current of nine $AgFeO_2$ materials

Material notation	Synthesis temperature (ºC)	NaOH mass (g)	Crystal Structure of delafossite	Particle morphology	OER current at 2.2 V vs. RHE (A/g)
AF1	115	1	2H + 3R	50-100 nm, rounded particles	18.7
AF2	115	1.6	2H + 3R	50-100 nm, rounded particles	16.1
AF3	115	2	2H + 3R	50-100 nm, rounded particles	16.3
AF4	155	1	2H + 3R	50-100 nm, rounded particles	19.2
AF5	155	1.6	3R	aggregates with sub-µm particles	15.4
AF6	155	2	3R	up to 5 µm, faceted crystals	11
AF7	155	2.4	3R	up to 5 µm, faceted crystals	10.6
AF8	180	1	2H + 3R	50-100 nm, rounded particles	13.7
AF9	180	1.6	3R	up to 5 µm, faceted crystals	8.8

4. CONCLUSION

In summary, we have synthesized $AgFeO_2$ delafossite materials via the hydrothermal method and investigated their electrocatalytic activity for the OER in 0.5 M KOH electrolyte. The phase structure and morphology of synthesized materials were characterized. It has been observed that 3R-$AgFeO_2$ material consists of microparticles while 3R/2H-$AgFeO_2$ materials are composed of nanoparticles. As a result of the comparison of OER activity of different delafossite materials, it was seen that the electrocatalytic activity of oxygen evolution reaction was higher in mixed-phase (3R/2H) materials. Consequently, it was determined that the delafossite phase structures affected the electrocatalytic activity. The origin of electrochemical activity difference is unknown to us at the moment and there are only a handful of studies in literatüre that looked into the disparity between the two polymorphs of delafossite materials. It is our thought that this study will pave avenues for the investigation of the relationship between phase structures and electrocatalytic activity on a larger scale.

ACKNOWLEDGEMENT

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DECLARATION OF ETHICAL STANDARDS

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission

AUTHORS’ CONTRIBUTIONS

Muharrem Kunduracı: Conceptualization, funding, writing the original draft.

Özkan Görmez: Synthesis.

Barış Saçlı: Synthesis.

Doğan Çirmi: Characterization, editing.

Uğur Çağlayan: Characterization.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

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