

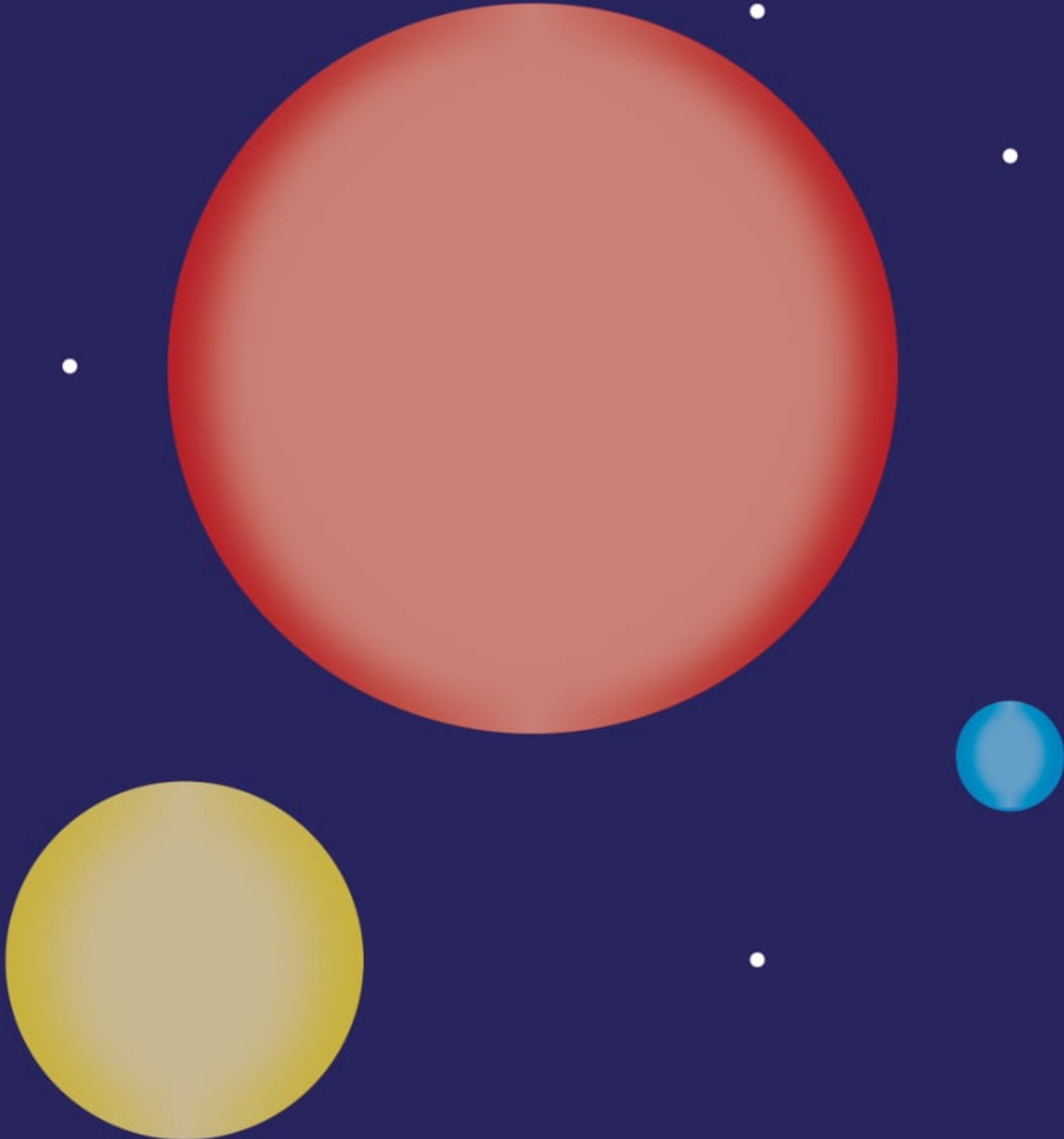


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Synthesis of Reduced Graphene Oxide (rGO) Supported Pt Nanoparticles via Supercritical Carbon Dioxide Deposition Technique for PEM Fuel Cell Electrodes

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Abstract

In this work, the preparation of reduced graphene oxide (rGO) supported Pt nanoparticles by using the supercritical carbon dioxide (scCO₂) deposition technique is investigated. For this purpose, firstly, graphite oxide synthesis was made similar to the literature reports and then two different reducing agents (DMF and hydrazine hydrate) were used to prepare rGO support materials, called as rGO1 and rGO2, respectively. Finally, Pt nanoparticles (NPs) were formed on the rGO support materials. The effect of the reducing agent type and also of the catalyst preparation technique on the fuel cell performance were examined with spectroscopic, microscopic, and electrochemical techniques. From the results obtained, it appears that the properties of rGO vary significantly depending on the reducing agent used. Moreover, the electrode containing Pt/rGO1 has exhibited better cell performance compared to the Pt/rGO2.

Key Words: PEM fuel cell electrodes, Pt nanoparticles, support material, reducing agent.

PEM Yakıt Pili Elektrotları için Süperkritik Karbondioksit Depozisyon Tekniği ile İndirgenmiş Grafen Oksit (rGO) Destekli Pt Nanoparçacıklarının Sentezi

Özet

Bu çalışmada, süperkritik karbondioksit depozisyon tekniği (scCO₂) kullanılarak indirgenmiş grafen oksit destekli (rGO) Pt nanoparçacıklarının sentezi araştırılmaktadır. Bu amaçla, öncelikle, literatüre benzer olarak grafit oksit sentezi gerçekleştirildi ve daha sonra iki farklı indirgeyici ajan (DMF ve hidrazin hidrat) ile sırasıyla rGO1 ve rGO2 olarak isimlendirilen rGO destek malzemeleri hazırlandı. Son olarakta, Pt nanoparçacıkları (NPs) rGO destek malzemeleri üzerine oluşturuldu. İndirgeyici ajan türünün ve katalizör hazırlama tekniğinin yakıt pili performansı üzerindeki etkisi spektroskopik, mikroskopik ve elektrokimyasal tekniklerle incelendi. Elde edilen sonuçlardan, kullanılan indirgeyici ajana bağlı olarak rGO malzemesinin özelliklerinin önemli ölçüde değiştiği görülmektedir. Ayrıca, Pt/rGO1 içeren elektrot, Pt/rGO2'ye kıyasla daha iyi pil performansı sergilemiştir.

Anahtar Kelimeler: PEM yakıt pili elektrotları, Pt nanoparçacıkları, destek malzemesi, indirgeyici ajan.

1. Introduction

Fuel cells are one of the important clean energy converting devices. Polymer electrolyte membrane fuel cells (PEMFCs) are the most studied among all types of fuel cells, especially for stationary, portable and automotive applications. It is mainly because of their high energy conversion efficiency, high energy density, low operation temperature, fast start-up and response times and low emission [1-4]. However, there are some critical obstacles preventing the commercialization and common usage of PEM fuel cells, such as high cost of platinum (Pt) catalysts and low durability of the catalyst layer [5-9]. For this reason, many strategies have been developed to increase catalytic activity and to reduce the usage of Pt-based catalysts. One of these strategies is to use carbon-based material as catalyst support [10-13]. Because support material not only provides conductivity but also provides a high surface area to improve the Pt utilization efficiency. Up to now, many alternative carbon-based materials such as carbon nanotubes, carbon aerogels, mesoporous carbon, fullerene, graphitic and carbon fibers have been tried as support materials [3, 14-20]. But, none of these prevalently used support materials can exactly fulfill the essential requirements. Hence, efforts must be put in for the development of new catalyst support.

In the past several years, graphene, with unrivalled 2D structure and properties including high conductivity, high specific surface area, high tensile strength, and etc., has been regarded as an alternative catalyst support for Pt nanoparticles (NPs) due to these superior features, have been commonly studied [21-26]. In literature, numerous methods have been developed to prepare graphene, including mechanical exfoliation of graphite (scotch-tape method), epitaxial growth, chemical vapor deposition, liquid phase exfoliation of graphite, chemical reduction of GO [27, 28]. Among all these methods, the chemical reduction of GO is the most promising method for mass production of graphene and this method involves of oxidation/reduction steps [29, 30]. Typically, graphite material is converted to GO via strongly oxidizing agents such as HNO₃, H₂SO₄, H₃PO₄, KMnO₄ and this oxidation step results in the widening of intersheet spacing of carbon layers due to the emplacement of functional groups onto the layer [31]. Following oxidation step, GO becomes hydrophilic in nature due to the polar oxygen functional groups and as a result, GO is easily dispersible in various solvents, especially in water [30]. The Van der Waals forces weaken because oxygen groups are

introduced in GO structure which results in a partial degradation of the sp^2 lattice into a sp^2 - sp^3 sheet with less π - π stacking ability. These changes make GO non-conductive as it lacks the conducting graphitic network. The conducting property of GO can be recovered by the reduction process, such as chemical reduction (e.g. via reducing agents) and thermal reduction (e.g. via annealing at high temperature under inert gas), which eliminates functional groups. The efficiency of the reduction process can be measured with O/C ratio and this ratio decreases significantly after reduction process. Also, according to the literature reports, in the high electrical conductivity required applications, it is necessary to reduce the O/C ratio below 1% [2]. However, in some cases, partially reduction also is desired, because the surface functional groups on the material serve as the anchoring sides for metal NPs while preventing restacking and aggregation to graphite form during the chemical reduction to graphene. Therefore, many studies are conducted in the literature on the preparation of Pt NPs onto the graphene-based materials such as graphene nanoplatelets (GNPs), graphene nanosheets, rGO, and functionalized graphene (g-GO) [2, 24, 32-34].

Along with the catalyst support material used, the catalyst preparation technique is also momentous and among the proposed catalyst preparation techniques in the literature, $scCO_2$ deposition technique has attracted attention in last years, due to its important advantages [8, 35-37]. This technique employs the dissolution of a metal precursor in the $scCO_2$ environment leading to the adsorption of the precursor into the support. Later, the metal precursor is converted to the corresponding metal via ex-situ or in-situ ways [38]. Thereby, supported metal NPs are obtained.

In most of the earlier reports on the Pt/rGO catalysts, on one hand, Pt NPs were formed on support during the reduction process of graphite oxide (GO), on the other hand, common techniques were used to create Pt NPs on the support. In our work, firstly, production of rGO support materials were achieved by using two different reducing agents and then Pt NPs were employed over these supports materials by using $scCO_2$ deposition technique. As far as we know, the decoration of Pt NPs on rGO support materials with the help of this technique and their fuel cell performances is presented in the literature for the first time. So, we believe that our study will make important contributions to the literature.

2. Material and Methods

2.1. Materials

STREM brand 1,5-dimethyl platinum cyclooctadiene (PtCODMe₂) was purchased for using as Pt organometallic precursor. Natural graphite flakes (average particle size 325 mesh) were procured from Alfa Aesar and used as received. Potassium peroxodisulfate (K₂S₂O₈ ≥99.9%), phosphorous pentoxide (P₂O₅, ≥98%), sulfuric acid (H₂SO₄ 98%), sodium nitrate (NaNO₃ ≥99.9%), potassium permanganate (KMnO₄ ≥99.9%), hydrogen peroxide (H₂O₂, 30%) were purchased from Sigma-Aldrich for use in GO synthesis and same brand dimethylformamide (DMF) and hydrazine hydrate were used as GO reducing agents. All chemicals were used without any further treatment. Also, high purity CO₂, N₂, O₂, H₂ gases were purchased from Habaş.

2.2. Preparation of Graphite Oxide (GO), Reduced Graphene Oxide (rGO) Materials

Firstly, GO synthesis was made from natural graphite powder by using improved synthesis proposed by Kovtyukhova et al. [39]. Subsequently, the GO was reduced with two different reducing agents (DMF and hydrazine hydrate) to obtain rGO materials. The details of the rGO synthesis procedure via DMF is described in our earlier report [40] and the resulting product was called as rGO1 in this study.

On the other hand, hydrazine hydrate material was also used as a reducing agent to the synthesis of rGO. Briefly, 0.5 g of dried GO was thoroughly dissolved in 0.5 L of water with the help of an ultrasonic bath until there was no visible particle in the solution. Subsequently, 5 mL of reducing agent was added into the solution and the reflux system was connected for the reduction process. The solution refluxed for 18 h at 100 °C. When the reflux process was completed, floating black particles were observed on the solution, which is due to the reduction of GO. Lastly, the solution was cooled down to room temperature, filtered and washed several times with water and methanol, respectively. After evaporation of the solvents with the rotary evaporator, the final product was obtained was called as rGO2.

2.3. Synthesis of rGO Supported Pt NPs

Pt NPs were created on the rGO support materials by using scCO_2 deposition method in a high pressure vessel. The details of synthesis procedure were mentioned in our previous studies [37, 41, 42]. To eliminate similarity, the schematic view of the experimental setup was shown in Fig. 1.

2.4. Characterization of the Materials

2.4.1. Characterization of physical properties

The surface structure parameters of the support materials were analyzed with BET isotherms by using the Micromeritics 3Flex analyzer. The samples were degassed at 90 °C for 12 h before taking measurements. Thermogravimetric (TG) analysis was performed using a Netzsch thermal analyzer with the heating rate of 10 °C/min and the flow rate of 30 mL/min in aluminum crucibles under air atmosphere. The Raman spectra of the pristine graphite, rGO1 and rGO2 materials were measured by using a WITech alpha 300R Raman system. Surface morphology and chemical composition of the support materials were observed by Zeiss Sigma 300 model scanning electron microscope (SEM), which is equipped with energy-dispersive X-ray spectroscopy (EDS). The homogeneity of the Pt NPs on the support materials were analyzed through the JEOL 2100 JEM transmission electron microscopy (TEM). TEM samples were prepared by dispersing supports and catalyst materials in ethanol to form a homogeneous suspension. Then, the suspension was dropped on copper grid for observation.

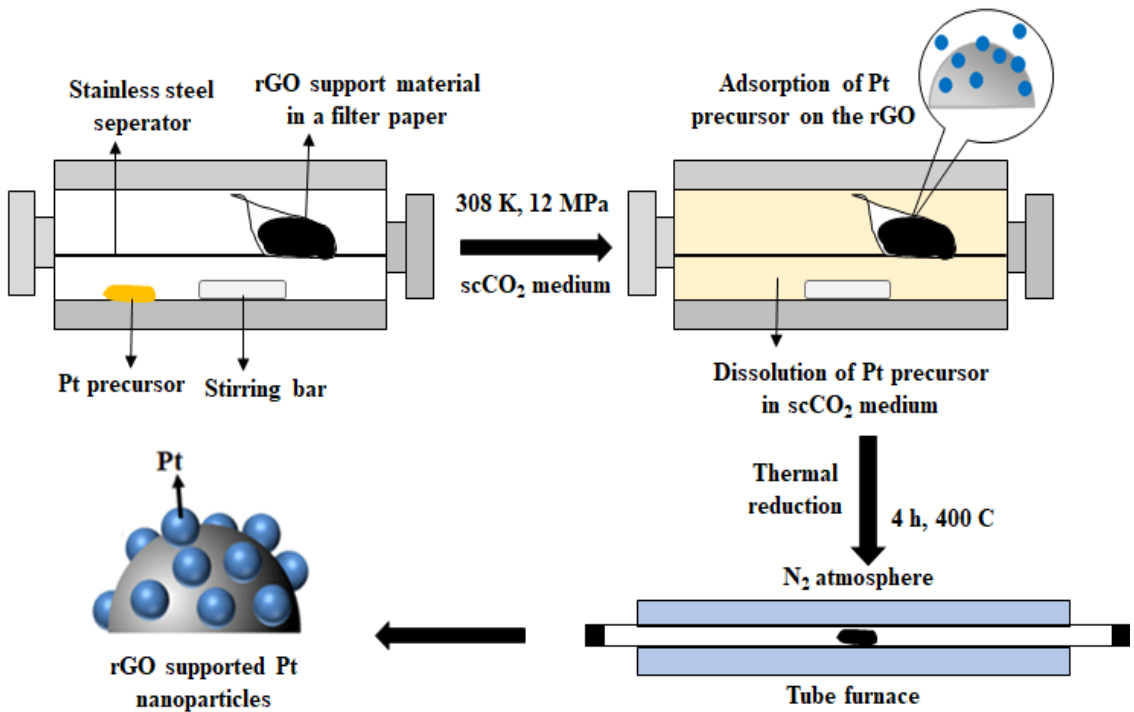


Figure 1. Experimental setup used for the decoration of Pt NPs on rGO support materials

2.4.2. Characterization of electrochemical properties

The ex-situ electrochemical studies of the support materials were performed in a standard three-electrode cell, using a VersaStat potentiostat/galvanostat. A silver-silver chloride electrode (Ag/AgCl, Cl⁻) with 3.5 M KCl solution as a reference electrode, a Pt wire as a counter electrode and glass carbon (GC) as working electrode were employed. The obtained cycling voltammograms were converted and presented in terms of normal hydrogen electrode (NHE). To prepare working electrode catalyst ink, the required amount of the support material, deionized water, 1,2-propanediol and 15% Nafion solution were mixed till obtaining uniform ink. Then, the ink was dropped on the GC with a micropipette and left to dry at the room environment. The amount of the material on the GC was maintained as 22 µg/cm² for each electrode.

Cyclic voltammetry (CV) measurements for hydrogen oxidation reactions (HOR) were carried out in a N₂ saturated 1 M H₂SO₄ electrolyte (potential range: 0-1.2V, scan rate: 50 mV/s). Then, in order to apply electrochemical oxidation, the electrode was subjected to a constant potential of 1.2 V for 24 h. At the end of 24 h, the same test procedure was repeated. Thus, the oxidation characteristics of the rGO1 and rGO2 materials were evaluated before and after the electrochemical oxidation treatment. The tests were repeated several times for both support materials until the same results were obtained.

2.5. Fabrication of Membrane Electrode Assembly (MEA) and Fuel Cell Tests

The in-situ electrochemical tests were performed in a single fuel cell system (Henatech™). Firstly, cathode and anode electrodes were prepared. The details related to electrode preparation by using the spraying method can be found in our previous papers [4, 9]. The Pt loading was set to 0.4 mgPt/cm² for all catalyst layers. Then, prepared electrodes were hot pressed at 130 °C and 400 psi for 3 min on to the Nafion 212 membrane to obtain MEA which has 4.41 cm² active surface area. Finally, the catalytic activities of MEAs were tested in a commercial PEM fuel cell test station. Hydrogen gas was fed from the anode side and oxygen gas fed from the cathode side, respectively. However, before the delivery of hydrogen and oxygen to the system, the cell was purged with nitrogen gas for a while. Meanwhile, the temperature of the cell and humidifier columns were adjusted to 70 °C. Subsequent to the purging, reactant gases were sent to the system. Then, polarization curves were taken by sweeping the voltage between OCV and 0.1V. In these measurements, the cell was equilibrated for at least 1 min at each point.

3. Results and Discussion

In heterogeneous catalysts, the vast majority of reactions take place on the catalyst surface. Therefore, it is very essential to accurately determine the surface area of the catalyst support. Likewise, the porosity and surface area knowledge of different support materials are of great importance in understanding their structure, formation, and potential applications. Surface area measurements are mainly carried out by the method of Brunauer, Emmett, and Teller (BET) [43]. According to this method, when a solid surface is reacted with a gas, the gas molecules attach to the surface and form adsorbed layers. The amount of adsorption is proportional to the total surface area of the sample. To determine the textural and structural properties of prepared support materials (rGO1 and rGO2), BET analysis was performed. The detailed BET results of rGO1 support material were given in our previous paper [40]. Hence, Fig. 2 shows the N₂ adsorption/desorption isotherms of the rGO2 support material and the corresponding pore size distribution. The isotherm of the rGO2 support material can be identified as type IV according to the International Union of Pure and Applied Chemistry (IUPAC) classification. Type IV isotherms are characteristic of materials containing mesopores and it shows a hysteresis loop from P/P₀=0.5 to P/P₀=1.0 which is H3 type hysteresis according to the IUPAC classification. This is attributed to the characteristic of aggregates of plate-like particles giving rise to slit-shaped pores and is common for carbon-like samples [44, 45].

According to the obtained BET results (Table 1), the surface area of the pristine graphite with a layered structure was found to be 13.7 m²/g [40]. After the chemical oxidation process, it was observed that the material structure changed and a decrease in the surface area (3.3 m²/g) occurred. Furthermore, after the reduction of GO with two different reducing agents, it was observed that the surface area values and pore volume values increased. However, the obtained surface area values were lower than the theoretical value (2630 m²/g) of single graphene sheet. This is attributed to the restacking phenomenon of the graphene sheets owing to strong van der Waals forces.

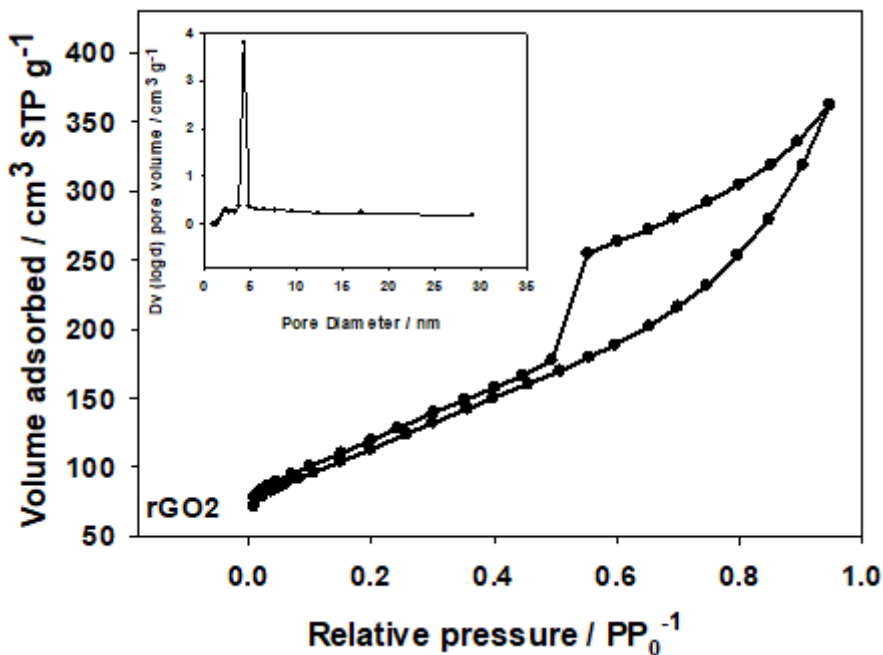


Figure 2. BET-N₂ adsorption/desorption isotherm and pore size distribution of the rGO2 support material

Table 1. Surface areas, pore volumes and pore sizes of the materials

Support	Total Surface Area (m ² /g)	BJH Pore Volume (cc/g)	BJH Average Pore Size (Å Diameter)	Ref.
Graphite	13.7	0.0270	22.4	[40]
GO	3.3	0.0095	31.3	[40]
rGO1	41.0	0.0513	22.5	[40]
rGO2	484.0	0.5050	22.2	(this study)

The thermal stabilities of the support materials were analyzed by TGA as shown in Fig. 3 (a). All measurements were carried out in air atmosphere up to 1000 °C. In both support materials, the initial weight loss was observed between 250-500 °C and this loss can be attributed to the gasification of the carbonaceous material due to oxidation of rGO [40]. Above 500 °C, almost a constant weight was observed up to 1000 °C and both support materials showed very similar trend in weight loss by temperature. Also, the Pt loading amount of the catalysts were calculated from the weight percent loss difference between rGO supports and the Pt/rGO catalysts (Fig. 3 (b-c)). The calculated Pt loading (wt.%) values were given in Table 2 and it was observed that the Pt loading on rGO1 support was 25.2%, while the loading on rGO2 support was 20%.

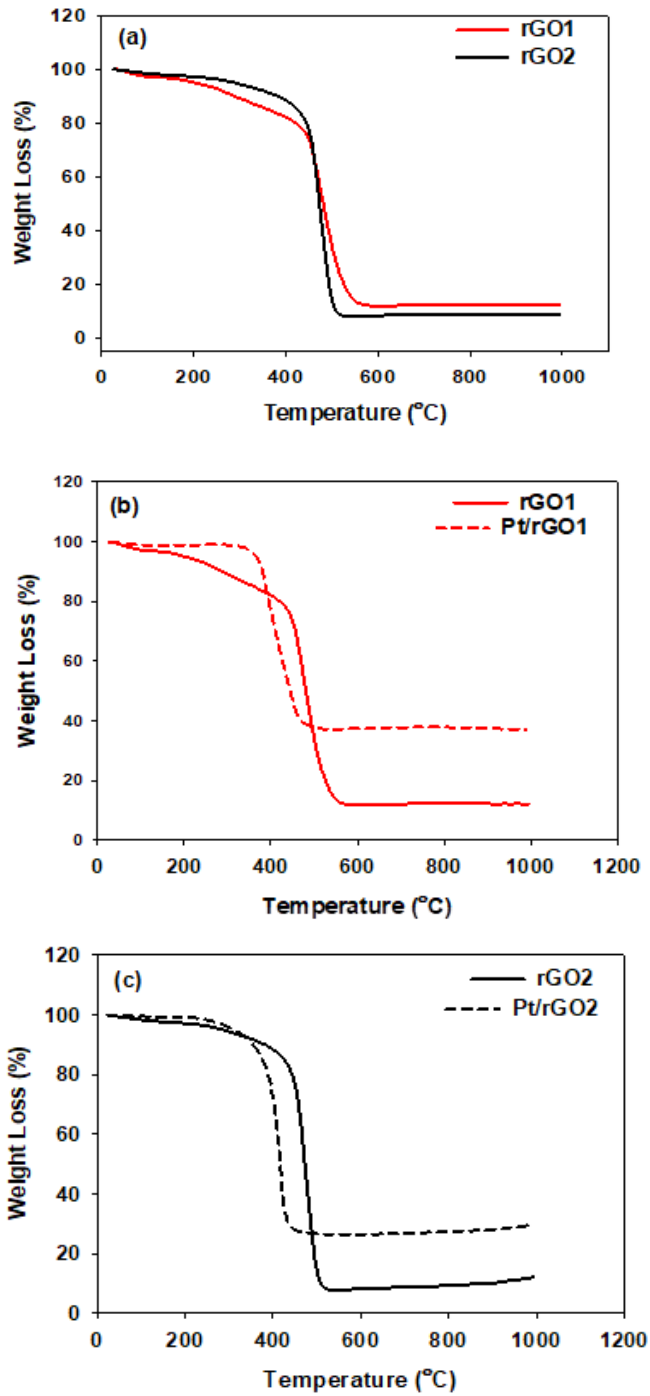


Figure 3. TGA curves of synthesized supports and catalysts

Table 2. Pt loading amounts of the catalysts

Catalyst	Pt [wt.%]
Pt/rGO1	25.2
Pt/rGO2	20

The morphology of the prepared support materials was investigated by using SEM. The obtained SEM plan-view images and corresponding EDS spectras were given in Fig. 4. The starting material was flake graphite having a flat morphology as shown in Fig. 4 (a). After the chemical oxidation process of graphite, the smooth flat structure turned into a rough and porous structure (Fig. 4 (b)). Also, the oxygen content increased owing to the formation of the oxygen functional groups on the edges and the basal planes of the rGO structure. In addition to the C and O atoms, the presence of new atoms such as S, K, Mn, Na were observed in the structure. Subsequently, the reduction process was carried out by using two different chemical reduction routes (as decribed in experimental part). Fig. 4 (c-d) shows the SEM images and corresponding EDS spectrums of the obtained rGO materials. As seen in the Fig. 4 (c), the rough surface structure of the GO changed into more uniform structure after reduction by DMF at reflux condition. Also, the purity of the material was checked by means of EDS and the spectra revealed that the structure still contain some residual impurities. In Fig. 4 (d) case, hydrazine hydrate was used to reduce GO. The obtained images showed that the structure contains micron-sized well-dispersed wrinkle flakes.

Fig. 5 displays TEM images of the rGO support materials and catalysts under different magnifications. In Fig. 5 (a) image, the rGO1 support material resembles a transparent ultrathin structure comprising few thin ripples within the plane, which is remarkably different from the opaque and smooth resemblance of pristine graphite flakes. This transparency and rippled characteristic of material, suggests that the material consists of a few thin layer or monolayer. Due to the wrinkled and overlapped structure, the individual graphene sheets can effectively link together and serve as great electrical conductor, resulting in high electrical conductivity [46]. On the other hand, the TEM image (Fig. 5 (b)) of rGO2 support material is composed of micrometer-sized wrinkled flakes with a high-transparency chiffon like texture. This wrinkle feature of the material prevents the aggregation of the dried sample due to van der Waals forces and play an important role in increasing the surface area [47].

Additionally, the TEM images of rGO supported Pt catalysts were also taken and results were given in Fig. 5 (c-d). It was clearly observed that the Pt NPs with spherical shaped particles were dispersed homogeneously on the rGO support materials. These results suggested that the scCO₂ deposition technique is a very accomplished method on the preparation of Pt NPs on rGO support materials.

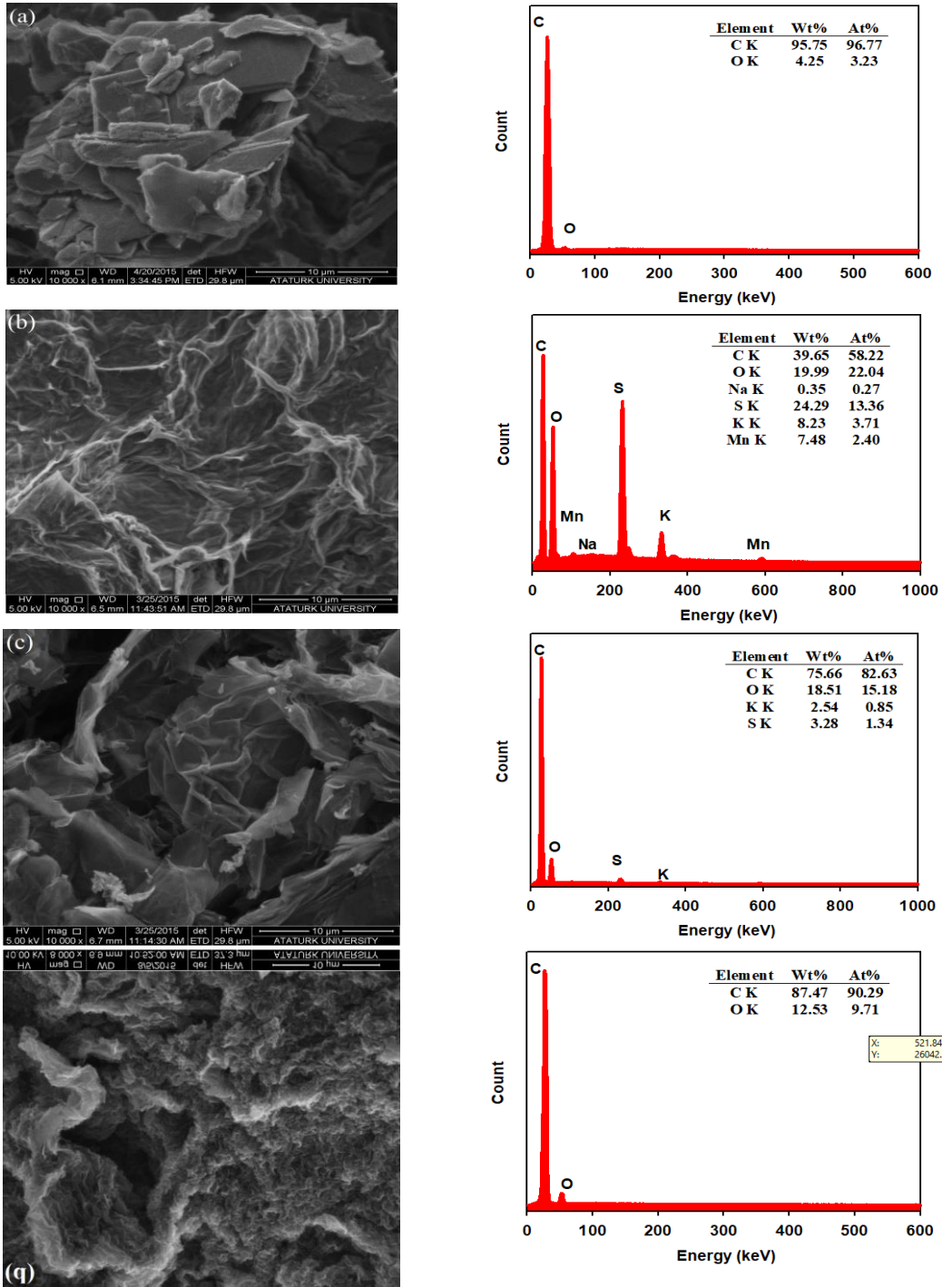


Figure 4. SEM and EDS results of (a) pristine graphite (b) GO (c) rGO1 (d) rGO2

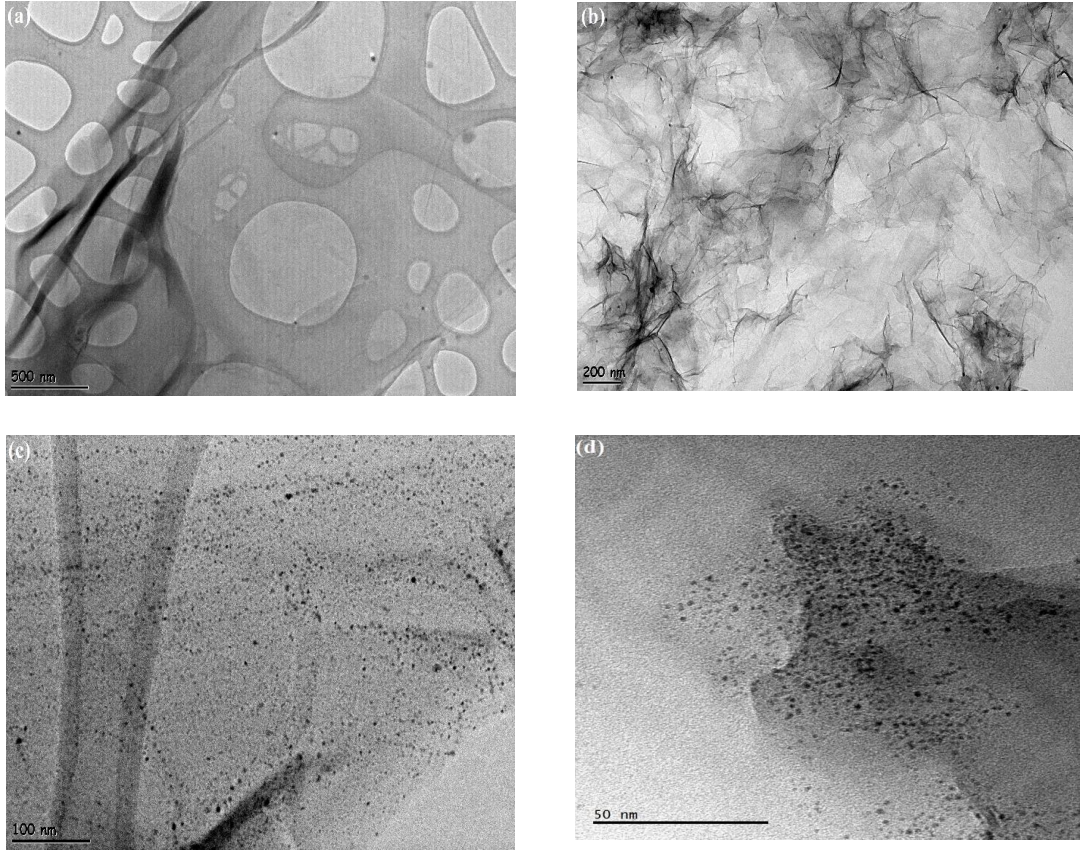


Figure 5. TEM images of (a) rGO1 (b) rGO2 (c) Pt/rGO1 (d) Pt/rGO2

Raman spectroscopy is an important characterization method used to evaluate the reduction effect and the main vibration peaks of carbon-based materials. Therefore, the pristine graphite and rGO support materials were characterized by Raman spectroscopy, as shown in Fig. 6. Two main characteristic peaks were observed for all the samples as D and G band. These bands are attributed to the defect/disorder states and the sp^2 -bonded in plane vibration of carbon atoms, respectively [29, 48]. For the pristine graphite, the D and G band positions are centered at 1346 and 1572 cm^{-1} respectively, while for rGO1 and rGO2, these bands are centered at 1352 and 1593 and at 1352 and 1591 cm^{-1} respectively. The band positions and intensity ratios (I_D/I_G) of materials are summarized in Table 3.

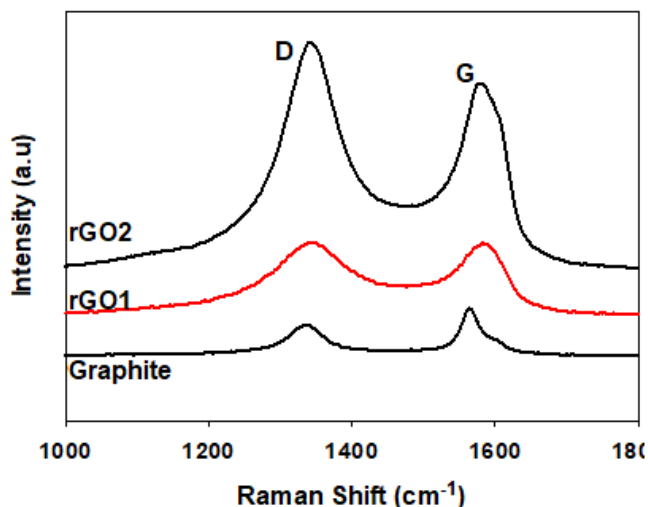


Figure 6. Raman spectra of pristine graphite, rGO1 and rGO2 support materials

Table 3. Analyses of Raman spectra

Sample	D band (cm ⁻¹)	G band (cm ⁻¹)	I _D /I _G
Graphite	1346	1572	0.48
rGO1	1352	1593	0.88
rGO2	1352	1591	1.22

As shown on Fig. 6 and Table 3, the Raman peaks showed change in band shape and band position. In the case of rGO, it appears that the D band position of both rGO material is almost unchanged. However, the G band position of rGO's exhibit a shift toward higher wavenumber compare to the pristine graphite, which attributes to the restoration of the sp² bond of the carbon structure.

The intensity ratio (I_D/I_G) of these bands provides important information about the level of the disorder. The I_D/I_G ratio of graphite, rGO1 and rGO2 materials was found to be 0.48, 0.88 and 1.22 respectively. The high intensity ratio reveals that the defects increase after the reduced process. This increase of I_D/I_G upon GO reduction is normal and could be attributed to the generation of edge atoms in the structure and also residual oxygen containing groups, vacancies and topological defects from degraded functional groups.

On the other hand, a number of activity losses are observed in the catalyst and catalyst support materials under harsh operating conditions of PEM fuel cells. These losses are usually caused by reason such as fuel starvation, poor water management, CO poisoning in the anode electrode. If the fuel in the anode is insufficient, the voltage rises up to the value needed to oxidize the water to maintain the current. However, such a high potential leads to carbon corrosion and metal dissolution, causing the anode catalyst layer to degrade. Therefore, the use of corrosion-resistant materials is of great importance. For this purpose, the cyclic voltammetry measurements were carried out to examine the electrochemical oxidation (carbon corrosion) of rGO materials. The obtained voltammograms were shown in Fig. 7. The electrochemical oxidation tests were performed by applying 1.2 V in both support materials for 24 h. The voltammograms were performed in the range of -0.1 to 1.1 V against the normal hydrogen electrode (NHE). In both support

materials, faradaic peaks were observed at around 0.6 V of anodic scan and around 0.55 V of cathodic scan, corresponding to redox reactions of surface functionalities which provide pseudocapacitance. However, these anodic and cathodic peaks become more pronounced after the electrochemical oxidation. Furthermore, the peaks are shifted to higher and lower values after the electrochemical oxidation. Similar findings were observed for many carbon-based support materials which is reported in the literature [12, 49, 50] and ascribed to the dependence on the surface concentration of hydroquinone/quinone redox couple [51]. Also, it was seen that the CV currents have increased after reduction process for both support materials, which reflect surface area changes as well as the formation of new surface oxide groups, is correlated with the extent of carbon corrosion [50], although the exact relationship is not clear. According to the obtained CV results, it can be said that the rGO1 exhibits better electrochemical properties compared to rGO2 support.

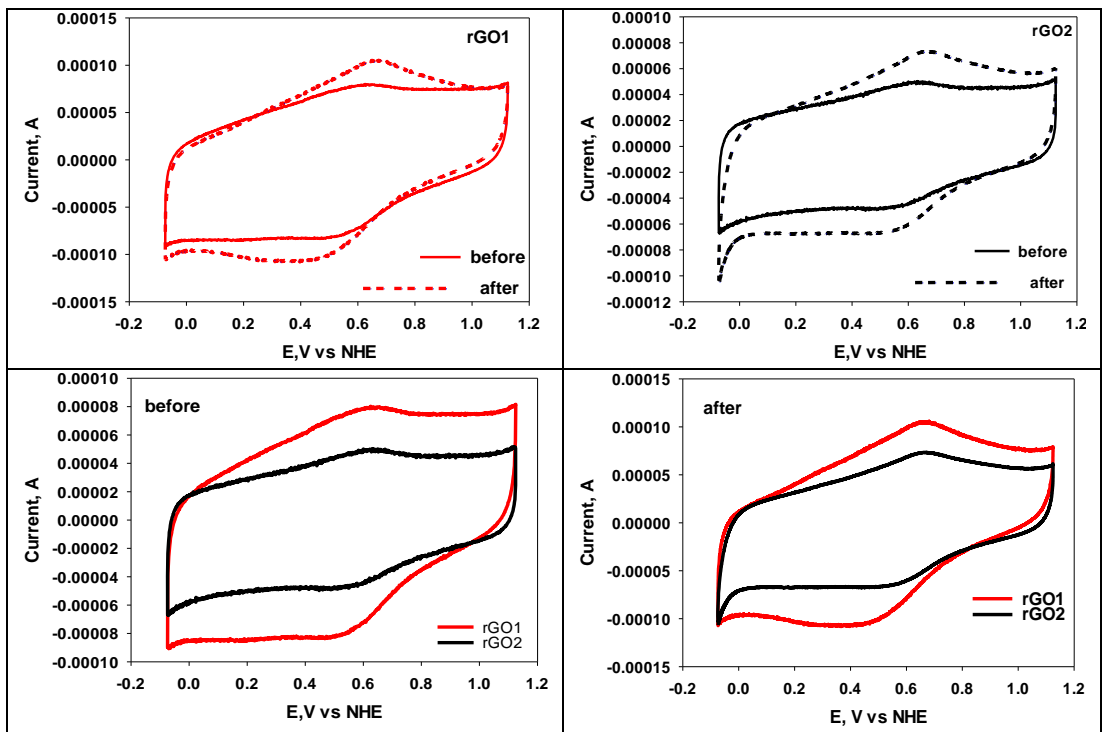


Figure 7. Cyclic voltammograms for rGO1 and rGO2 support materials before and after electrochemical oxidation

Fuel cell performances were also evaluated by using a single cell test station and the obtained polarization curves were given in Fig. 8. It was observed that the performance of the catalyst prepared with rGO1 support is higher than that of the rGO2 supported catalyst, especially at high current density region. This high fuel cell performance can be attributed to the structural properties of rGO1 support material, which provides superior mass transfer capability for reaction species compared to the rGO2 support material. The maximum power density achieved with the Pt/rGO1 catalyst is approximately 635 mW/cm^2 and higher than those reported maximum power density values for Pt/rGO (320 mW/cm^2) [52], Pt/rGO (375 mW/cm^2) [2], the partially GO-Pt (161 mW/cm^2) [25].

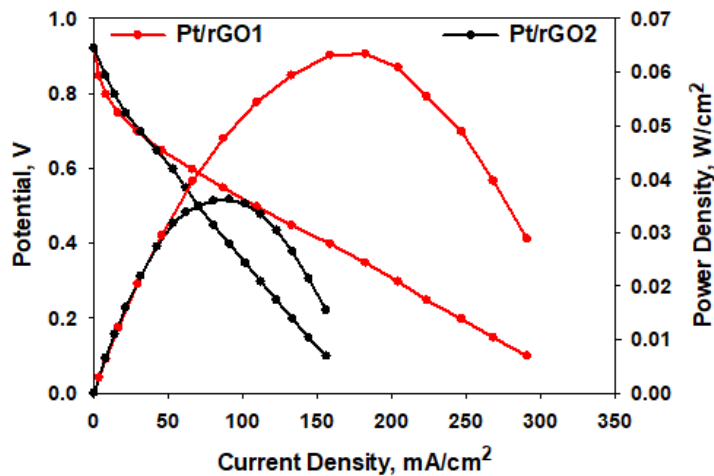


Figure 8. PEM fuel cell polarization curves

4. Conclusion

In summary, we have demonstrated a facile and effective method for the preparation of rGO supported Pt NPs catalysts. Firstly, synthesis of rGO support materials were achieved by using two different reducing agents and then Pt NPs were created over these support materials by using scCO_2 deposition technique. To the best our knowledge, this is the first example of rGO supported Pt NPs where Pt NPs were decorated on the support by using scCO_2 deposition technique. The physicochemical and electrochemical experimental results showed that reducing agents used in the rGO support materials significantly affect the properties of the support materials and also PEM fuel cell performances. The maximum power density of 635 mWcm^{-1} was achieved with Pt/rGO1 catalysts.

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Conflicts of interest

The authors declare that there are no potential conflicts of interest relevant to this article.

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Spectral Disentangling of Binary Stars: ϵ Lupi

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Abstract

In this study, which is based on spectral disentangling in binary systems, ϵ Lupi (HD 136504) has been studied. ϵ Lupi is a double-lined spectroscopic binary system (SB2) consisting of two early type B stars. A total of 575 spectra of ϵ Lupi downloaded from the PolarBase database were used for spectral disentangling. Before spectral disentangling, we cleaned telluric lines, merged orders, normalized the continuum of spectra. To obtain individual spectra of the components, FDBinary code was used. Consequently, the spectra of the components of the ϵ Lupi system were separated in the wavelength range 3920 - 8560 Å. The radial velocities and atmospheric parameters of the primary and secondary components will be found using with the resultant normalized spectra of ϵ Lupi.

Key Words: Binary stars, Spectral disentangling, ϵ Lupi, Spectral analysis.

Çift Yıldızlarda Tayfsal Çözümleme: ϵ Lupi

Özet

Çift yıldız sistemlerinde tayfsal çözümleme konusunu ele alan bu çalışmada, ϵ Lupi (HD 136504) yıldızı incelenmiştir. ϵ Lupi iki erken tür B yıldızından oluşan çift çizgili tayfsal çift (SB2) sistemdir. Tayfsal çözümleme için ϵ Lupi'ye ait PolarBase arşivinden indirilen toplam 575 tayf kullanılmıştır. Çift sisteme ait bileşen tayfları ayırmadan önce tellürik çizgileri temizleme, tayf parçalarını(order) birleştirme, süreklilik normalizasyonu vb. işlemler uygulanmıştır. ϵ Lupi'ye ait bileşen tayfların ayrı ayrı elde edilmesi için FDBinary kodu kullanılmıştır. Sonuç olarak, ϵ Lupi'nin bileşen tayfları 3920 - 8560 Å dalgaboyu aralığında ayrılmıştır. Bu çalışma sonucunda ϵ Lupi'nin bileşenlerine ait normalize tayflar kullanılarak dikine hızlar ve atmosferik parametreler bulunabilir.

Anahtar Kelimeler: Çift yıldızlar, Tayfsal çözümleme, ϵ Lupi, Tayf analizi.

1. Introduction

Son yıllarda çift yıldızların analizi için birçok yöntem geliştirilmiştir. İlk olarak 1994 yılında Simon & Sturm yaptıkları çalışma ile yörünge faz aralığını kapsayan gözlemlerden çift çizgili tayfsal ikiliden bileşen yıldızla ait olan tayfı çıkarabildiği tayfsal çözümleme (SPD) tekniğini bulmuştur [1]. Bu teknik SPD çizgilerinin iç içe geçmesinden etkilenmeyen tayfsal yörüngeleri ölçmek için kullanılmaktadır. Ortaya çıkan ayrık tayflar ayrıca orijinal gözlemlerden çok daha yüksek bir sinyal/ gürültü oranına (S/ N) sahiptir, bu da onları kimyasal bolluk analizi için çok yararlı kılmaktadır [2]. Daha sonra Hadrava tarafından 1995 yılında önerilen ve iç içe geçmiş (kompozit) tayfların ayrılması için DFT (Discrete Fourier Transform) yöntemi kullanılmıştır [3]. Bu çalışmanın ardından Sasa Iljic (2003) çift yıldızların iç içe geçmiş tayflarının çözümlemesi için FDBinary kodunu geliştirmiştir [4]. Unix işletim sistemi için C programlama dilinde yazılan bu kod, Fourier alanında çalışmaktadır.

Thackeray'a göre [5], ϵ Lupi keşfi, Lick Southern Gözlemeviden 1907-1911 yılları arasında alınan 10 plaka görüntüsü ile Paddock tarafından yapılmıştır [6]. Ancak başkaları tarafından tek hız ölçümleri yapılırken 1907'de H.D. Curtis [7], çift çizgilerin dikine hızlarını (Radial Velocity RV) ölçerek kaydetti. Böylece ϵ Lupinin çift çizgili tayfsal çift yıldız olduğu gözlemlendi. 1964 yılında Radcliffe Gözlemevinde tayf gözlemleri kullanılarak ϵ Lupinin yörünge parametrelerini elde etmek için çalışmalara başlandı. ϵ Lupinin çift çizgili davranışına rağmen üretilen ilk yörüngesi bulunmuştur. ϵ Lupinin yörünge parametrelerinin belirlenmesini zorlaştıran üç durum vardı: (i) Alınan iki tayfın farklı akıda olması, (ii) sistemin bir yörünge döneminin çeyreğinden daha az zamanda, 100 km s^{-1} daha fazla olması, (iii) bileşenlerin ayrıklığının 160 km s^{-1} aşmayan hızlara sahip olması. Bunlara rağmen Thackeray (1970) Radcliffe tayflarını kullanarak ϵ Lupi'ye ait yörünge parametrelerini elde etmiş ve bu parametreler Tablo 1'de verilmiştir. Tablo 1'de baş ve yoldaş yıldızla ait P (dönem) değerinin olması sistemin tutulma göstermemesinden ve sadece tayfsal çift sistem olmasından kaynaklanır.

Tablo 1: ϵ Lupi sisteminin Thackeray (1970) tarafından bulunan yörünge parametreleri.

Parametreler	Baş yıldız	Yoldaş yıldız	Toplam sistem
P	4.559794±0.000013	4.559748±0.000026	4.559783 gün
T ₀			39370.68±0.09
γ	+7.4±1.94	+6.6±3.7	+7.9±1.4 km s^{-1}
K ₁	56.5±2.3		56.1±1.5 km s^{-1}
K ₂		65.3±2.8	64.8±1.8 km s^{-1}
e	0.28±0.045	0.21±0.06	0.26±0.03
ω_1	324±11		330±10°
ω_2		171±24	
T	2439370.64±0.10	2430370.85±0.24	2439370.68±0.09

2. Material and Methods

Çift sistemlerin bileřenleri optik teleskoplarla dođrudan gözlemlenemez ve çözülemez. Fotometrik olarak ayrılabilen bazı görsel çift yıldızlar bileřen tayflarının ayrı ayrı kaydedilmesine izin vermeyebilir [4]. Çift yıldız sistemlerinin hemen hemen hepsinde bileřen yıldızların parlaklıđı çok farklı olmadığı müddetçe gözlenen tayf her iki bileřene ait özellikler barındırır. Yörünge dönemi boyunca düzenli zaman aralıklarında alınan bu tayflar, bileřen yıldızların dikine hızlarının yörünge dönemine bađımlılıđı ve tayf özellikleri hakkında bilgi içerir.

Bileřen yıldızların kütlelerinin belirlenmesi için sistemdeki bileřenlerin yörünge hareketi nedeniyle tayf çizgilerindeki kaymalara bakılır. Ölçülen dikine hız profillerine uygulanan Gauss fiti yapılması gibi basit yöntemler ve çapraz korelasyon (cross-corelation) teknikleri gibi o kadar basit olmayan yöntemler standart dikine hız ölçüm araçları olarak kabul edilir [8]. Ancak çizgilerin karışması, bileřen karışıklığı, sinyal/ gürültü oranı gibi zorluklar bu tür ölçümler için engel teşkil eder. Çapraz korelasyon tekniđinin uygulanması ile büyük bir ilerleme yaşanmıştır. Ancak bu tekniđin dahi (üretilen sentetik tayflar veya belirli tayf türüne ait olan bilinen bir yıldızın tayfı gibi şablon tayflara olan ihtiyaç vb.) dezavantajı vardır. Yüzey sıcaklıklarının belirlenmesi veya yıldız atmosferindeki kimyasal element bolluklarının incelenmesi gibi durumlarda sistemdeki bileřen yıldızların tayflarına ihtiyaç vardır. Elde edilen bu karma karışık bilgiler içeren tayf çizgilerinin ayrılması ve çözülmesi gerekir. Bu zorlukları gidermek için kullanılan bazı yöntemler vardır.

Bunlar; (i) Spektroastrometrik Yarıлма (Spectroastrometric Splitting), (ii) Tayfsal Ayırma (Spectral Separation), (iii) Tayfsal Çözümle (Spectral Disentangling) [9]. Yıldız tayflarını ayrı ayrı elde edebilmek ve yörünge parametrelerini daha dođru bir şekilde hesaplayabilmek adına bu çalışmada tayfsal çözümleme tekniđi baz alınmıştır.

2.1. Tayfsal Çözümleme (Spectral Disentangling, SPD)

SPD ile iç içe geçmiş tayfların ayrılması, sadece bileřen yıldızların tayflarının yeniden yapılandırılmasına deđil, aynı zamanda yıldız sisteminin yörünge parametrelerinin belirlenmesine yönelik bir uygulamadır.

Yörünge elemanlarını elde etmek için ilk uygulamalarda bile, SPD tekniđinin diđer yöntemlerden daha üstün olduđu bulunmuştur [1][10,11]. Sistemin iç içe geçmiş (kompozit) tayflarının her bir bileřen tayfı için dođru ışık faktörleri yani bileřenlerin toplam ışınımına ne kadar katkıda buldukları ve dikine hızları bilinmelidir. Bu bileřenler bilindiđi takdirde iç içe geçmiş tayfların yeniden yapılandırılması ve bileřenlerine ayrılması mümkündür. Işık faktörleri, ışık eğrilerinin analizi ile belirlenebilir. Dikine hızlar, Gaussları iyi çözülmüş çizgilere yerleştirilmesi gibi geleneksel teknikler yoluyla veya iki boyutlu çapraz korelasyon yoluyla dođrudan iç içe geçmiş tayfta ölçülebilir.

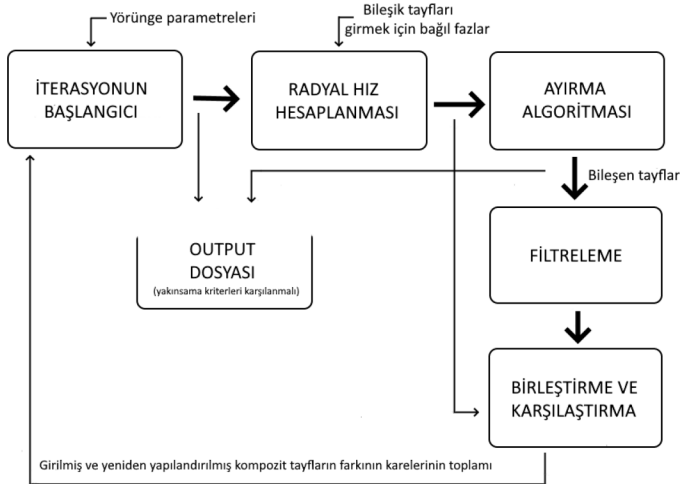
İç içe geçmiş tayfların ayrılması için ışık oranı hakkında önceden bir bilgi sahibi olmamız gerekmez ancak dikine hızların yanlış belirlenmesi bileřen tayfları çözerken büyük bir sorun teşkil eder. Bu nedenle, dođru dikine hızlar, yıldız sisteminin bireysel bileřenlerinin tayflarını yeniden yapılandırmak için gereken iç içe geçmiş tayflar olan verilerin ikinci en kritik kısmı olarak düşünülebilir. SPD ile ölçülen yörüngeler tutarlıdır ve karmaşık çizgiler için herhangi bir düzeltme

gerekmez. Bu bakımdan SPD tekniđinin uygulanması teřvik edicidir. Bu yzden bu alıřmada ϵ Lupi sistemine SPD tekniđi uygulanmıřtır.

2.2. FDBinary Kodu

FDBinary, ift yıldızların i ie gemiř tayflarının ayrılması ve özölmesi iin kullanılan aık kaynaklı bir koddur. SPD dikine hızları kullanarak Fourier uzayında uygulanır. Ayrıca Keplerin yörünge elemanlarından beř parametreye bađlıdır: (i) bileřenlere ait dikine hız yarı genliđi, (ii) dıř merkezlik, (iii) genel bir evre kayması ve (iv) enberi boylamı. Yörünge hareketlerini aıklayan bu parametrelere ek olarak iki parametre kullanılabilir. Bu iki parametre ise Gözlenen girdi tayfları ve yörünge dönemidir. Gözlenen girdi tayfları, dalgaboyunda seilen aralıklarla logaritmik ölekte örneklendirilmelidir. Yörünge dönemi, gözlemlenen her bir tayfta belirlenmelidir.

SPD tekniđinin uygulanmasında kullandıđımız *FDBinary* kodu hız uzayında ve matris formatında alıřır. Bu kodu farklı zamanlarda ve farklı dalgaboyu aralıklarında alınmıř ift yıldız sistemine ait bileřke tayflarını ayrı ayrı elde edilmesini sađlar. *FDBinary* kodunun akıř řeması řekil 1’de verilmiřtir.



řekil 1. FDBinary kodunun akıř řeması

FDBinary kodu girdi (input) ve ıktı (output) dosyalarından oluřur. Girdi dosyasında verdiđimiz parametrelere göre bu kod iterasyon yaparak ıktı dosyasını oluřturur ve bize bileřen yıldızlara ait ayrılmıř tayfaları verir.

eps_lup_master.obs	8.27104	8.28172	eps_lup	1	1	0							
5634.148410	0	0.01	1	1									
5634.149530	0	0.01	1	1									
5634.149120	0	0.01	1	1									
6819.869530	0	0.01	1	1									
6819.870250	0	0.01	1	1									
6819.870950	0	0.01	1	1									
6819.872030	0	0.01	1	1									
6819.871570	0	0.01	1	1									
6819.872390	0	0.01	1	1									
6819.873110	0	0.01	1	1									
6819.873830	0	0.01	1	1									
6819.874910	0	0.01	1	1									
6819.874550	0	0.01	1	1									
6819.875270	0	0.01	1	1									
6819.875900	0	0.01	1	1									
6819.876700	0	0.01	1	1									
6819.877770	0	0.01	1	1									
6824.871160	0	0.01	1	1									
6824.871870	0	0.01	1	1									
6824.872590	0	0.01	1	1									
7121.989940	0	0.01	1	1									
7121.989330	0	0.01	1	1									
7121.990560	0	0.01	1	1									
7121.991800	0	0.01	1	1									
7121.993050	0	0.01	1	1									
7121.994910	0	0.01	1	1									
7235.817390	0	0.01	1	1									
7235.818630	0	0.01	1	1									
7235.819860	0	0.01	1	1									
1	0	0	0	0	0	0							
4.559783	0	5649.26251	0.085001	0.27	0.00	383.712184	0	53.935776	0.0	64.3919179	0.0	0	0
100	1000	0.00001											

Şekil 2. ϵ Lupi'ye ait FDBinary için hazırlanan input dosyası.

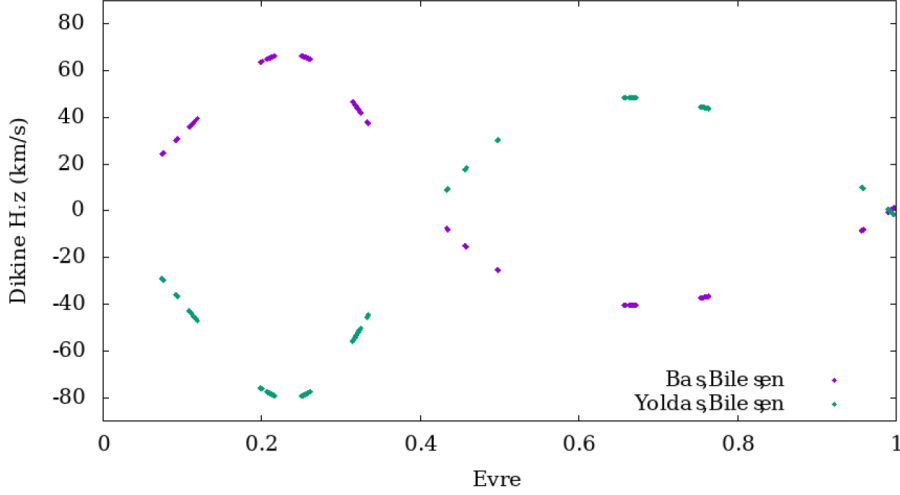
Oluşturulan girdi dosyası, gözlenen tayflar için yörünge parametreleri ve girilen ilk değerler gibi tanımlayıcıları içeren kontrol dosyasıdır. Zamanlar gün, hızlar km s^{-1} ve açılar derece cinsindedir. Şekil 2'de verilen örnek girdi dosyasının içinde bulunan 'eps_lup_master.obs' isimli dosyada sisteme ait gözlenen tayflar bulunur. Bu dosyada, çift sisteme ait tayfların dalgaboyuna (logaritmik ölçekte) karşılık normalize akı değerlerini içeren matris formatında veriler bulunur. 'eps_lup' ise çözümleme için kullanılan dalgaboyu aralığındaki gözlemleri içeren çıktı (output) dosyasıdır. Şekil 2'de bulunan pembe kutunun içindeki değerler sırasıyla gözlem tayfları, çözümleme yapılacak dalgaboyu aralığı, çıktı dosyası ve yıldız sistemine ait bileşen değerleridir. Kırmızı kutunun içinde tanımlananlar gözlenen tayfa ait özellikleri içerir. Sırasıyla sütunlarda bulunan değerler: gözlemlere ait Jülyen günü (JD), güneş merkezli dikine hız düzeltmesi, hata payı, baş yıldızın ışık faktörü ve yoldaş yıldızın ışık faktörü. Mavi kutunun içindeki değerler üçüncü bileşene ait değerlerdir. Yeşil kutunun içindeki değerler iç yörüngeye ait parametreleri içerir. Bu değerler; dönem (P), başlangıç zamanı (T_0), dış merkezlik/basıklık (e), yıldızın koç noktasından enberi noktasına olan açısı (ω), baş yıldızın dikine hızı (K_1) ve yoldaş yıldızın dikine hızı (K_2) şeklindedir. Son olarak mor kutunun içindekiler ise sırasıyla kalibre sayısı, iterasyon ve toleranstır.

SPD yapılacak olan yıldızın ait parametreler ile oluşturulan girdi dosyasının hazırlanmasıyla *FDBinary* kodu çalıştırılır. Bu kod verilen ilk değerleri kullanarak iterasyon yapar ve çift yıldızın ait tayfları ayırır. Bu işlemin tamamlanmasıyla bu kod bize ayrılmış tayflara ait çıktı dosyalarını verir.

3. Tartışma ve Bulgular

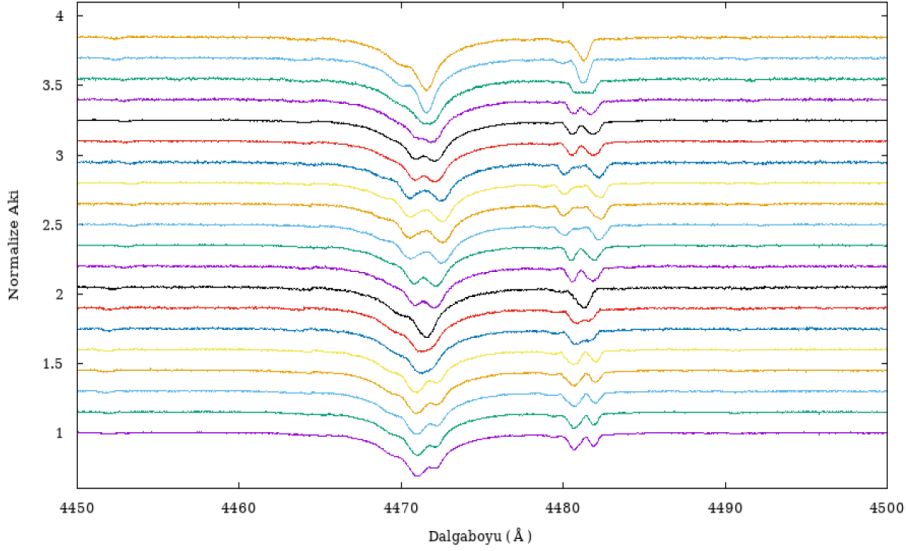
PolarBase yıldız arşivinden sıcaklıkları 10000-40000 K arasındaki çift yıldız sistemlerini incelenmiştir. İncelenen bu yıldızlardan SPD için uygun görülen ϵ Lupi çift yıldız sistemi üzerinde çalışmaya karar verilmiştir. PolarBase yıldız arşivinden ϵ Lupi'ye ait normalize edilmemiş tayflara ait veriler indirilmiştir. İndirilen verilerden Jülyen günleri ile Tablo 1'deki sonuç sütununda yer alan P ve T_0 değerlerini alarak *FDBinary* sonucunda elde ettiğimiz dikine hızlar ile ϵ Lupi'ye ait tayfların evre

dađılımına gre dikine hızları hesaplanmıřtır (řekil 3). ift yıldızların iki bileřeninden aynı anda 0.25 ve 0.75 evrelerinde tayf bilgisi alındıđından dolayı ϵ Lupi'nin bu evreler civarından tayfının olup olmadıđını kontrol edilmiřtir. Evre dađılımını iyi anlayabilmek iin hesaplanan evrelerin dikine hız eđrisi oluřturulmuřtur.



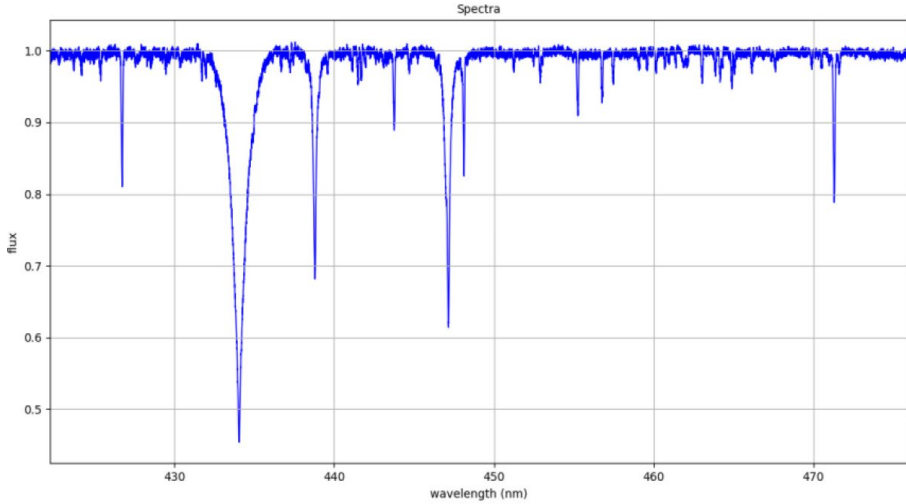
řekil 3. PolarBase arřivinden indirilen 575 tane tayf kullanılarak oluřturulan ϵ Lupi'ye ait dikine hız eđrisi. Sistemdeki bař(mor) ve yoldař(yeřil) bileřene ait tayf izgilerinin dikine hız lmleri verilmiřtir. x-ekseninde evreye karřı y-ekseninde dikine hız deđerleri verilmiřtir.

Tayfsal ayırmanın ilk ařaması olarak, ϵ Lupi'ye ait indirdiđimiz tayfların iindeki verilerde eksiklik olup olmadıđı incelenmiřtir. Bunun sonucunda 568 tayfın kullanılabilir olduđuna karar verilmiřtir. Bu tayfları normalize etmek iin yazmıř olduđumuz normalizasyon kodu kullanılmıřtır. Bu kodu kullanmadan nce iSpec yardımıyla ϵ Lupi'ye ait atom izgilerinin tayf zerindeki konumlarını dalgaboyuna gre belirleyerek izgi listesi oluřturulmuřtur. Oluřturduđumuz bu izgi listesini, atom izgilerinin srekliliđinin bozulmaması iin normalizasyon kodunda kullanılmıřtır. Normalizasyon koduyla: (i) Atmosferden kaynaklı etkilerden oluřan tellrik izgileri tayftan temizledik, (ii) srekliliđi bulmak iin tayf paralarının (order) akı deđerinin maksimum ile minimumdaki dalga boyunu ve medyan deđerlerini belirledik, (iii) belirli dalgaboyu aralıklarındaki tayf paralarına sırasına gre normalize ettik. Normalizasyon sonucu elde ettiđimiz tayf paralarını birleřtirilirken bazı sorunlar meydana geldi. Birleřmiř tayfta, tayf paralarının kenarları st ste gelerek srekliliđin akı kalınlařmasına neden oldu. Bu sorunu giderebilmek iin tayf paralarını dalgaboyuna gre kırıplmıřtır. Ardından tayf paralarının ortalamasını ve medyanını alarak tekrar normalize edilmiřtir. En sonunda tm tayf paraları birleřtirilmiřtir. Birleřtirdiđimiz tayf paraları řekil 4'te sunulmuřtur.



Şekil 4. ϵ Lupi'ye ait farklı evrelerde alınmış 20 tayfin dalgaboyuna karşılık normalize akı grafiđi. Burada Helyum (4471 Å) ve Magnezyum II (4481 Å) çizgilerinin evreye göre deđiřimi rahatlıkla fark edilmektedir.

Normalize ettiđimiz tayfları incelediđimizde Balmer Serisinin iyi bir řekilde normalize olmadıđını fark ettik. Bu durum Balmer çizgilerinin geniř olmasından kaynaklanır. Bu etkinin sonucunda süreklilik normalizasyonunda kaymalar meydana gelir. Bu sorunun giderilmesi için hidrojen çizgilerine farklı bir normalizasyon işlemi uyguladık. Örnek olarak Şekil 5'te yeniden normalize edilmiş H γ çizgisi iSpec üzerinden gösterdik.

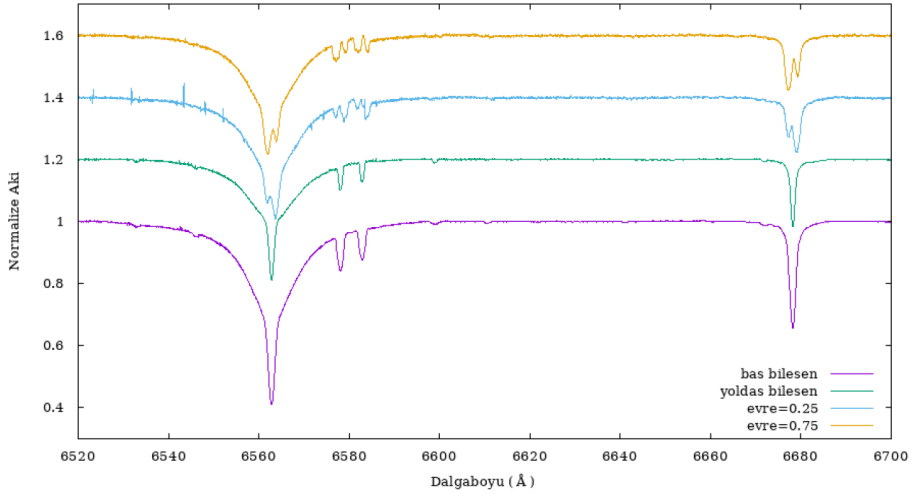


Şekil 5. Yeniden normalize edilmiş H γ çizgisinin dalgaboyuna (wavelength) karşılık akı (flux) deđerinin iSpec arayüzünde gösterimi. Dalgaboyu nanometre (nm) birimindedir. H γ çizgisi 434.1 nanometreye karşılık gelir.

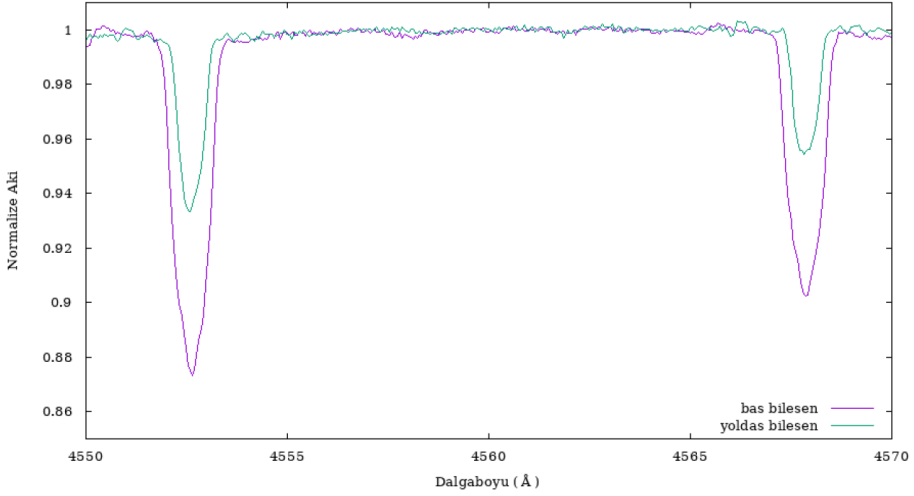
ϵ Lupi sistemine ait yıldızların tayflarını ayrı ayrı elde etmek için incelenen tayfların *FDBinary* programında kullanılacak formata dönüřtürdük (Ayrıntıları için bkz. bölüm 2.2). *FDBinary* kodu için Şekil 1'deki gibi girdi dosyalarımızı oluřturduk. Bu dosyalar oluřturulurken bileřenlerin ışığa katkı oranları bilinmediđinden ikisi içinde ışık faktörü ($I_f = 1.0$) deđerini aldık. ϵ Lupi'nin normalize edilmiş

tayfını en fazla 30 Å dalgaboyu aralıklarında bölerek kodu çalıştırdık. Bu işlemi Balmer serisi için de ayrıca yaptık. *FDBinary* kodu ile girilen parametrelere göre belirlediğimiz dalgaboyu aralığında iterasyon yaparak ϵ Lupi'nin bileşenlerinin tayfını ayrı ayrı elde ettik. Sonuç olarak *FDBinary* bize beş çıktı dosyası verdi: (i) '.obs' uzantılı bileşik tayfı, (ii) '.mod' uzantılı bileşen yıldızların ayrılmış tayflarını içeren model tayfı, (iii) '.res' uzantılı ayırma işlemi için belirlediğimiz dalgaboyu aralığındaki kalıntısı, (iv) '.rvs' uzantılı bileşenlerin dikine hız verileri ve (v) '.log' uzantılı yapılan işlemlerin kayıtlarının olduğu dosya. Elde edilen bu dosyalardan '.mod' uzantılı dosyadaki bileşenlere ait model tayfları ayırdık. Sürekliliği normalize etmek için öncelikle iSpec koduyla hazırlanmış gridlerden sentetik tayf oluşturduk. Bunun için B yıldızlarına özel hazırlanan BSTAR2006_TLUSTY sentetik tayf gridlerini kullandık [12]. Ayrıca ϵ Lupi'ye ait baş ve yoldaş yıldızın sırasıyla yüzey çekim ivmeleri $\log g_{Aa} = 3.97$, $\log g_{Ab} = 4.13$ ve etkin sıcaklıkları için sırasıyla $T_{eff Aa} = 20500$ K, $T_{eff Ab} = 18500$ K ile tayf çözünürlüğü için de $R = 85000$ piksel kullandık.

Oluşturulan sentetik tayfı *Java Multipegale* programında kullanarak, *FDBinary*'den elde edilen tayfların sürekliliğini normalize ettik. Bu işlem sırasında süreklilikteki çakışan kısımların fazlalıklarını atarak birleştirdik. Son olarak baş ve yoldaş yıldızın ait normalize edilmiş ve ayrılmış tayfları Şekil 6 ve Şekil 7'de örnek olarak çizdirdik.



Şekil 6. ϵ Lupi'ye ait 6520 - 6700 Å dalgaboyu aralığındaki ayrılmış tayfların baş yıldız (mor), yoldaş yıldız (yeşil) ve birleşik tayfın 0.25 (Mavi) ve 0.75 (Sarı) evreden alınan tayfları olmak üzere normalize akıya karşı dalgaboyu grafiği. Grafikte $H\alpha$ (6563 Å) ile He I (6678 Å) gösterilmektedir.



řekil 7. ϵ Lupi'ye ait FDBinary kodu ile çözdüđümüz Si III (4553 Å ve 4568 Å) sođurma çizgilerine ait normalize akı deđerine karřı dalgalıbyu grafiđi. Bař yıldız (mor) ve yoldař yıldız (yeřil) olarak çizdirdik.

4. Sonuç ve Öneriler

Çift yıldız sistemlerinde tayfsal çözümlene konusunu temel alan bu çalıřmada, iki erken tip B tayf türünden yıldız içeren ϵ Lupi (HD 136504) çift çizgili tayfsal çift sistemi kullanıldı. ϵ Lupi'nin evre dađılımlarının iyi olması ve daha önce tayfsal ayırma yapılmamıř olması bizim için iyi bir aday olduđunu gösterdi.

ϵ Lupi'ye ait farklı evrelerdeki gözlemlerden çift çizgili tayfsal çiftin bileřenlerine ait olan tayfı ayırılmak için tayfsal çözümlene (SPD) tekniđini uyguladıđ. SPD tekniđini uygularken iSpec programından ve *FDBinary* kodundan yararlandık. Bu çalıřma sonucunda ϵ Lupi sistemine uyguladıđımız çözümlene tekniđi ile bař ve yoldař bileřenlerin ayrı ayrı tayflarını elde ettik. Ayrıca Sisteme ait yörünge parametrelerini $K_1= 53.8914 \text{ km s}^{-1}$, $K_2= 64.6822 \text{ km s}^{-1}$, $e = 0.2723$, $T_0= 2439370.83 \text{ JD}$ ve $\omega= 383^\circ.1$ olarak hesapladık.

Çalıřma sonucunda elde edilen ayrılmıř tayflar kullanılarak yıldızların atmosferik parametreleri belirlenebilir. Ek olarak çalıřma sonucunda ϵ Lupi'ye ait normalize edilmiř tayflara LSD ve CCF yöntemlerini uygulayarak bileřenlerin dikine hızları hesaplanabilir. Bulunan dikine hızlarla bileřenlere ait kütleler elde edilebileceđi sonucuna varılmıřtır.

Çıkar Çatıřması

Yazarlar herhangi bir çıkar çatıřması olmadıđını beyan etmektedirler.

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JAPA

Investigation of Natural Silica Minerals from the Kizilirmak with EPR Spectroscopy

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Abstract

A silica mineral contained in gravel taking from the Kizilirmak deposit and bearing organic radicals in its structure was investigated by EPR spectroscopy. The type of radicals in the silica mineral determined under different temperatures and different microwave power were by examining the intensity distributions of the EPR lines. In EPR spectra, the signals with different intensity distributions were detected. g and A spin-Hamiltonian parameters for these signals were calculated and given in Table 1. These signals are attributed to the $\dot{C}H_2$, $\dot{C}H_3$, $\dot{C}H$, CO_2^- , O_3^- radicals in the glassy structure by comparing with the literature.

Key Words: EPR, Radical, Glassy structure.

Kızilirmak Yatağından Çıkarılan Doğal Silis Mineralinin EPR Spektroskopisi ile İncelenmesi

Özet

Kızilirmak yatağından alınan çakıl içinde bulunan ve yapısında organik radikaller bulunduran bir silis minerali EPR spektroskopisi ile incelenmiştir. Farklı sıcaklıklarda ve farklı mikrodalga gücü altında incelenen silis minerali içerisindeki radikallerin türü, EPR çizgilerinin şiddet dağılımlarına bakılarak belirlenmiştir. EPR spektrumlarında şiddet dağılımları birbirinden farklı olan sinyaller tespit edilmiş ve bu sinyallere ait g ve A spin-Hamiltonien parametreleri hesaplanmış ve Tablo 1'de verilmiştir. Literatür ile karşılaştırılarak, sinyaller camsı yapı içerisindeki $\dot{C}H_2$, $\dot{C}H_3$, $\dot{C}H$, CO_2^- , O_3^- radikallerine atfedilmiştir.

Anahtar Kelimeler: EPR, Radikal, Camsı yapı.

1. Introduction

The root of natural stones is based on the molten magma of the Earth's core, which constantly moves and always tries to reach the outer surface. Some of this extremely hot mass brings volcanic activity and lava flow. Magma often flows into underground cracks in the lower layer of the planet. Boiling water, steam and gases have also accompanied with the molten rock and minerals. It has been occurring the crystals and precious stones by combining with many minerals that accumulates in the cracks while gasses are become cold.

The surrounding mineral is shaped by pressure, heat and chemically acid or basic media. The small change in environmental conditions can even allow a mineral to grow, stop, change or even form a new one. This may cause to show different properties in the same mineral found in different places [1, 2]. There are many active fault lines in Turkey. There are many different natural phenomena and occurrences around these lines. For example, hot water sources and springs are in these regions. In addition to these, various geological events are also observed in these regions. Granites, syenite, monzonite, quartz diorite, biotite granites are present in the massifs along the Kızılırmak. Marble, fluorite, copper, zinc, chromite and magnesite were also detected in the region. One of these is the SiO_2 mineral in the glassy or the crystal forms (quartz, etc.), which is very common in nature. This mineral, in general called as silica or siliceous compound, present in pure form and it composes precious and semi-precious stones in different colors by keeping various metals in impurities, such as opal or amethyst.

Besides these well-known forms, well-known organic radicals can also be trapped within various silica composite located near moving fault lines as mentioned. There is no accurate information about the trapping mechanisms of most active organic radicals trapped in the cavities formed in the SiO_2 matrix. But the most comment one is, the trapped organic compounds which is in silica composite melted within the fossil deposits such as coal, natural gas or oil leaked due to hot magma approaching the surface in faults are fragmented by exposure to high-energy radiation as radiated from radioactive radon (or someone else) leaked from fault fissures. These chemically important and active radicals have continued their existence almost indefinitely since thousands, perhaps millions of years, despite being exposed to various natural conditions [1].

Electron paramagnetic resonance (EPR) spectroscopy is, as well known, a powerful technique for detecting and analyzing trace amounts of paramagnetic impurities at various temperatures. EPR deals only with transitions between spin states. It is not only the external magnetic field that is effective in spin transition. Local magnetic fields produced in the paramagnetic center also affect the spin transitions. The sources making up the local magnetic fields are the nuclei having non-zero spin and other paramagnetic centers located the orbit of the electron and near, which interacts with the paramagnetic ions. In this way, EPR gives detailed information about the orbit of the paramagnetic ion and its interacting nuclei. It can be comments on by taking advantage of the properties of the EPR spectrum such as line intensity, line position, line width and line splitting.

The hyperfine interaction between the magnetic moment of an electron and the magnetic moment of a nucleus can be studied with various experimental techniques [3]. In Electron Paramagnetic Resonance (EPR) spectroscopy, hyperfine interactions manifest as line splittings in the spectrum.

Such splittings, originating from copper nuclei with spin $I = 3/2$, have first been observed by R.P. Penrose in 1949 [4] in a single crystal of a copper doped magnesium tutton salt. Since then, measurements of hyperfine interactions with EPR have developed to an indispensable tool for the study of paramagnetic entities in single crystals, in polycrystals, and in frozen and liquid solutions [5-8]. Hyperfine data are particularly helpful in understanding the electronic and geometric structure of paramagnetic species. They enable one to draw up a detailed mapping of the electron spin density distribution, and contain precise information about the spatial arrangement of the nuclei close to the unpaired electron [9, 10].

Electron paramagnetic resonance (EPR) spectroscopy is, as well known, a powerful technique for detecting and analyzing trace amounts of paramagnetic impurities which is assumed to be reflecting the lattice structure of the host at various temperatures. In this study, the types of radicals are determined by examining a silica mineral containing organic radicals and located in pebbles taken from the bed of the Kızılırmak with an EPR spectrometer. This research is particularly interesting for those who work on natural formations, organic radicals, and spectroscopic techniques. It is estimated that the silica mineral was probably formed by the drift of Kızılırmak along the active North Anatolian fault line.

2. Materials and Method

Silica minerals containing organic radicals were extracted from the Kızılırmak deposit. Samples were cleaned to remove any contamination and sized appropriately for EPR measurements. EPR spectra of minerals are recorded in a magnetic field modulation frequency of 100 kHz by using a Varian E-104 X-band EPR spectrometer. The g values were achieved by comparison with a 2,2-diphenyl-1-picrylhydrazyl (DPPH) sample of $g = 2.0036$.

3. Results and Discussion

EPR spectroscopy is the most powerful tool known for examining and determining these important radicals, in trace amounts, in the minerals containing silicon dioxide and in the glassy structure. An X-band EPR spectrometer was used through the experimental work. The EPR spectra taken this glassy structure found in nature at room temperature shown in Fig. 1 and at 433 K in Fig. 2. The line widths of the signals represented by A and B are increased by rising the temperature to 433 K and therefore the line amplitudes are decreasing. By increasing the microwave power applied to the sample at this temperature, the EPR signals lost in the spectra due to the high Signal to Noise ratio have become evident.

When the permitted transitions are considered in the EPR, if an unpaired electron interacts with a nucleus having the spin I , $2I + 1$ lines with the identical EPR intensity distributions are observed. If there are n identical nuclei interacting with the unpaired electron, the $2nI + 1$ lines appear, whose intensities are not identical. EPR signal groups with different the intensity distributions were observed in the spectrum given in Fig. 2. Existing more than one radical group with the same intensity

distribution indicate that they are taking place in different chemical environments. The hyperfine spin-Hamiltonian has the form

$$\mathcal{H}_{hfs} = S\bar{A}I$$

In first order, the measured hyperfine angular frequency consists of two contributions, the isotropic Fermi contact term;

$$a_{iso} = \frac{8\pi}{3\hbar} g_e \beta_e g_n \beta_n \langle \psi_0 | \delta(r) | \psi_0 \rangle$$

and the electron-nuclear dipole-dipole coupling;

$$A_{ij}^{DD} = \frac{g_e \beta_e g_n \beta_n}{\hbar} \left\langle \psi_0 \left| \frac{3r_i r_j - \delta_{ij} r^2}{r^5} \right| \psi_0 \right\rangle$$

where ψ_0 is the orbital of the unpaired electron and r_i is a component of the radius vector from the electron to the nucleus. The spin-only coupling tensor A^{DD} is traceless and symmetric [11].

g values and superfine splitting constants (A) were found for every radical appears in this glassy. These values indicate which of the signal is belong to which radical. The measured g and A parameters are given in Table 1.

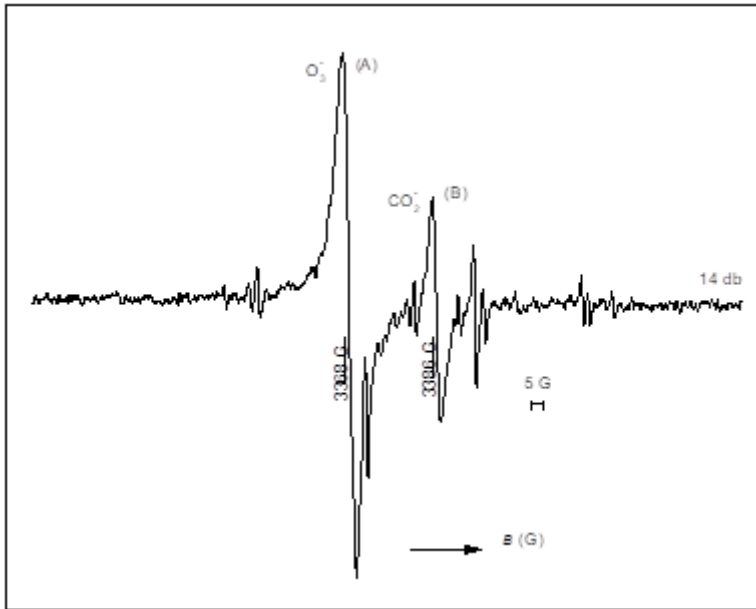


Figure 1. EPR spectrum of natural glassy at room temperature (microwave power= 14 dB).

From the calculated g values of the EPR lines marked as A and B and varied the line widths and intensities as depending on temperature, this EPR signals were determined that belong to O_3^- and CO_2^- radicals, respectively. The g values for these radicals are in agreement with the g values obtained in previous studies [12-14, 17, 22].

Table 1. Spin-Hamiltonien parameters of radicals in natural glassy structure.

Radical	$g \pm 0.0003$	$A_1 \pm 0.5$ (G)	$A_2 \pm 0.5$ (G)	Radical	$g \pm 0.0003$	$A_1 \pm 0.5$ (G)	$A_2 \pm 0.5$ (G)
A	2.0111	-	-	E	2.0024	8.75	-
B	2.0002	-	-	F	2.0026	22	-
C	2.0018	27	-	G	2.0011	123.5	-
D	2.0022	22.5	-	H	2.0033	76	5.5

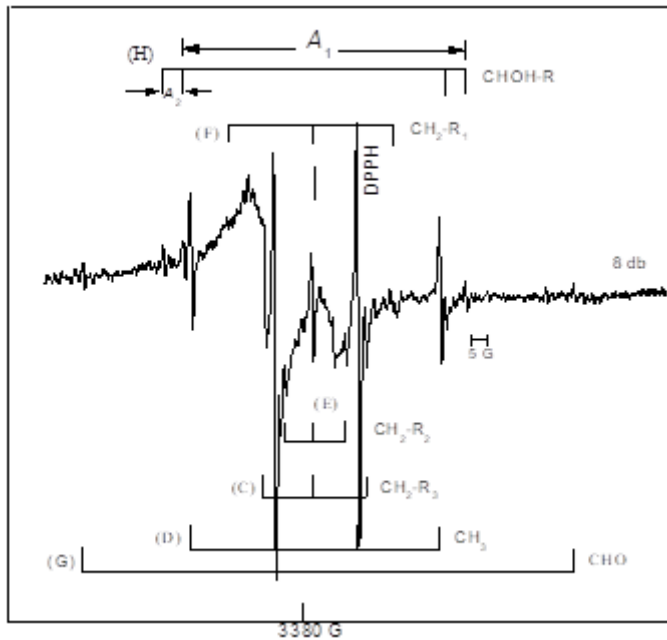


Figure 2. EPR spectrum of natural glassy taken at 433 K (microwave power = 8dB).

The quartet signal (D) shown in Fig. 2 and having a 1: 3: 3: 1 intensity distribution originates from three identical protons of the methyl ($\bullet \text{CH}_3$) group. The g and A values found for this signal is compatible with the literature for the $\bullet \text{CH}_3$ radical [13]. Although the methyl radical is extremely active and mobile, the silica continues its existence in the lattice since thousands of years.

The hyperfine structure splits of the two triplet signals (E and F) in Figure 2 are quite different from each other and the E and F signals have identical shape but belong to two different group in the structure. The g values calculated for these radicals are equal to each other. The difference of hyperfine structure splits is due to CH_2 radicals are linked to different inactive groups [15].

The doublet line indicated by "G" in Figure 2 with the hyperfine splitting of 123.5 G and $g = 2.0011$ belongs to \bullet HCO radical. The calculated values of g and A for this signal are in good agreement with the published data in the literature [16].

Another doublet with 27 G splitting and $g = 2.0018$ value appears in Fig. 2. This signal previously represented with a "C" belongs to the \bullet CH₂ radical attached to an inactive group R₃ [18-20]. "H" signal appearing as quadruple signals in the spectrum in Fig. 2 attributed to \bullet CHOH radical. The unpaired electron interacted with one of the non-identical protons and signaled the doublet. The unpaired electron then interacts with the beta proton to cause a doublet repeat splitting [20, 21].

4. Conclusions

The EPR spectra of the natural glassy structures containing silicon are given in Fig. 1 and Fig. 2. The g values of signals A and B in Figure 1 were determined as 2.0111 and 2.0002 and attributed to radicals O_3^- and CO_2^- , respectively. It was observed that the line widths and intensities of the EPR signals of these radicals changed with temperature. According to the g values of the EPR signals represented by C, D, E, F, G and H in Fig. 2, they can be assigned to the organic radicals \bullet CH₂, \bullet CH₃, CH₂-R₁, CH₂-R₂, \bullet HCO and \bullet CHOH respectively. The spin Hamiltonian parameters of each signal were found and are given in Table 1. The results show that this mineral was probably deposited by the Kızılırmak drifting along the active North Anatolian fault line.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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PHOTOMETRIC OBSERVATIONS of FOUR W UMA BINARIES

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Abstract

In this work, the light curves of NSVS2175434, V783 And, ASAS J020753+2034.1 and NR CAM W Uma type eclipsing binary star systems were obtained by using 0.5 meter ATA50 telescope in Atatürk University Astrophysics Research and Application Center (ATASAM). The orbital period variations of the systems were analyzed using the "timing" method. Only the O-C diagram of NR Cam was performed because the eclipse times of the other systems in the literature are not sufficient. When the O-C diagram of the NR Cam system is examined, no clear change has been observed for the time being. However, more observational data are needed to understand whether changes will occur in the future.

Key Words: Binaries, W Uma, Eclipsing stars

DÖRT W UMA ÇİFT YILDIZ SİSTEMİNİN FOTOMETRİK GÖZLEMLERİ

Özet

Bu çalışmada NSVS2175434, V783 And, ASAS J020753+2034.1 ve NR CAM W Uma tipi örten çift yıldız sistemlerinin Atatürk Üniversitesi Astrofizik Araştırma ve Uygulama Merkezi (ATASAM) bünyesindeki 0.5 metrelik ATA50 teleskobu ile elde edilen örtülme ışık eğrileri sunuldu. Sistemlerin yörünge dönem değişimleri "zamanlama" yöntemi kullanılarak incelendi. NR Cam dışındaki sistemlerin literatürdeki minimum zamanları yeterli olmadığı için sadece NR Cam'ın O-C diyagramı oluşturuldu. NR Cam sistemine ait O-C diyagramı incelendiğinde net bir değişime şu an için rastlanılmadı. Ancak ilerleyen zamanlarda değişimin olup olmayacağını daha net görebilmek için daha fazla gözlemsel veriye ihtiyaç vardır.

Anahtar Kelimeler: Çift yıldızlar, W Uma, Örtülme

1. Giriş

Gökyüzünde gördüğümüz yıldızların yarısından fazlası iki veya daha fazla yıldızdan oluşmaktadır. Bu tür sistemler çift yıldız olarak adlandırılmaktadır. Çift yıldız sistemleri, ortak kütle merkezi etrafında kütle çekim etkisi altında Kepler yasalarına göre yörünge hareketi yapan iki veya daha fazla yıldızdan oluşan sistemlerdir [1]. Çift yıldızlarda aralarındaki kütle çekim kuvvetinden yola çıkarak sistemdeki bileşenlerin ışınım gücü, yarıçap ve kütle gibi bazı temel parametreler hesaplanabilir. Bu parametreler yıldızların oluşum süreçleri ve evrim teorileri hakkında bilgi sahibi olmamıza yardımcı olur. Ayrıca, çift yıldızlar yıldız evriminin açıklanmasında, yakın galaksilerin uzaklıklarının belirlenmesinde, X-ışın çiftleri, kataklizmik değişenler, novalar, simbiyotik yıldızlar ve bazı tür süpernovaların açıklanmasında da önemli rol oynamaktadır. Bu nedenle çift yıldızlar, astrofizikte tekli yıldızlara nispeten daha çok bilgi sunmaları bakımından daha büyük bir öneme sahiptirler.

Çift yıldız sistemleri gözlemsel olarak keşfedilme ve incelenme yöntemlerine göre Görsel, Astrometrik, Tayfsal ve Örtten çift yıldızlar olarak sınıflandırılır. Örtten çift yıldızlarda, sistemdeki bileşenlerden birinin diğerinin önünden geçerken sistemin parlaklığında periyodik bir azalma meydana gelir. Bu nedenle bu tür çift yıldız sistemlerine “Örtten Değişen Yıldızlar” adı da verilmektedir [2, 3]. Örtten çiftler, ışık eğrilerinin şekillerine göre; Algol türü (EA), β Lyrae türü (EB) ve W Uma türü (EW) sistemler olmak üzere üç ana gruba ayrılırlar. W Uma türü sistemler; farklı kütlelerde, neredeyse aynı sıcaklıklara sahip, birbirine çok yakın ve her ikisi de Roch lobunu doldurmuş yıldızlardan oluşan çift yıldız sistemleri olup bu sistemler aşırı degen örtten çiftler olarak da bilinir [2, 4].

Son yıllarda, yapılan araştırmalar sonucunda çift yıldız sistemlerinin yörünge dönemlerinde periyodik olarak bir değişimin olduğu gözlemlendi [5, 6, 7, 8, 9, 10]. Bu araştırmalar çift yıldız sisteminin kütle merkezinin hareketinden kaynaklanan ve sistemdeki bileşenlerin karşılıklı olarak birbirlerini örtme zamanlarındaki periyodik değişimlerin ölçülmesi sonucu görülen LTT (the Light Travel Time) etkisinin incelenmesiyle yapıldı [8, 11]. LTT etkisi olarak yorumlanan sistemin tutulmalarının O-C (Observed-Calculated) zamanlarındaki periyodik değişimlere dayanan yöntem ise “zamanlama” yöntemi olarak adlandırılmaktadır. Bu çalışmada NSVS2175434, V783 And, ASAS J020753+2034.1 ve NR CAM olmak üzere dört örtten W Uma türü çift yıldız sisteminin minimum zamanları hesaplanarak yörüngesel dönemlerinde herhangi bir değişimin olup olmadığı “zamanlama” yöntemi kullanılarak incelendi.

2. Materyal ve Yöntem

NSVS2175434, V783 And, ASAS J020753+2034.1 ve NR CAM W Uma tipi örtten çift yıldız sistemlerinin gözlemleri, Atatürk Üniversitesi Astrofizik Araştırma ve Uygulama Merkezi (ATASAM) bünyesindeki 26.3'x26.3' görüş alanına sahip Apogee U230 2K CCD kamera ile 0.5 m'lik (ATA50) teleskop kullanılarak 15 Ekim 2021 ile 16 Kasım 2021 tarihleri arasında her bir kaynak için bir gece olacak şekilde gerçekleştirildi. Tüm sistemlere ait gözlemler, R ve/veya B filtrelerinde ve 20-60 sn aralığında poz süresi verilerek yapıldı.

Temel görüntü indirgeme verileri Bias, Dark ve Flat neredeyse her gözlem gecesi için ayrı ayrı alındı. Veri indirgeme işlemi Python (CCDDData, ccdproc, numpy, astropy, matplotlib ve glop gibi paketler) ve MaximDL programları kullanılarak yapıldı. Veri indirgeme işlemi sırasında standart Bias, Dark çıkarımı ve Flat düzeltmeleri yapıldı. Temel amacımız sadece fark ışık ölçümünü elde etmek olduğu için herhangi bir standart yıldız gözlenmedi. Fakat veri indirgeme süresince karşılaştırma yıldızı olarak kaynağa hem parlaklık hem de konum olarak en yakın yıldız kullanıldı (Tablo 1).

Tablo 1 Dört W Uma tipi örtlen çift yıldızın ve fark ışık ölçümü sırasında kullanılan referans yıldızına ait bilgiler [12]

Kaynak	Kadir	Referans	Kadir
NSVS2175434	13.80 (G)	TYC 4087-1801-1	10.72 (V)
V783 And	14.84 (R)	TYC 2781-920-1	12.44 (B)
ASAS J020753+2034.1	12.85 (V)	TYC 1220-1405-1	11.23 (V)
NR Cam	10.97 (V)	GSC 4531-1979	8.15 (V)

Bu işlemlerin ardından sistemlere ait örtülme ışık eğrileri elde edildi. Sistemlere ait yörünge zaman değişimlerinin incelenebilmesi için elde edilen ışık eğrileri Gauss (Denklem 1) ve Polinom (Denklem 2) fonksiyonları içeren bir fonksiyon (Gauss+Pol) ile modellenildi.

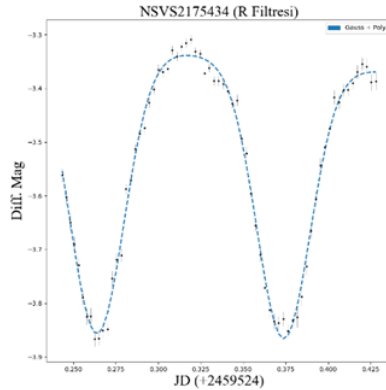
Gauss Fonksiyonu:

$$f(x; A, \mu, \sigma) = \frac{A}{\sigma\sqrt{2\pi}} e^{[-(x-\mu)^2/2\sigma^2]} \quad \text{Denklem 1}$$

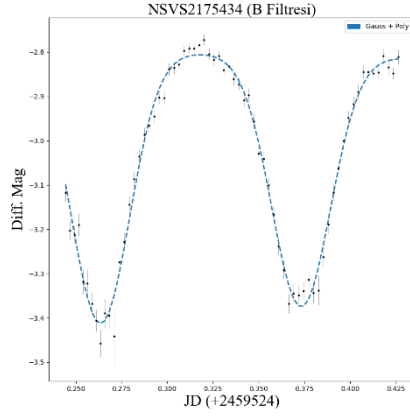
Polinom Fonksiyonu:

$$f(x; c_0, c_1, \dots, c_7) = \sum_{i=0,7} c_i x^i \quad \text{Denklem 2}$$

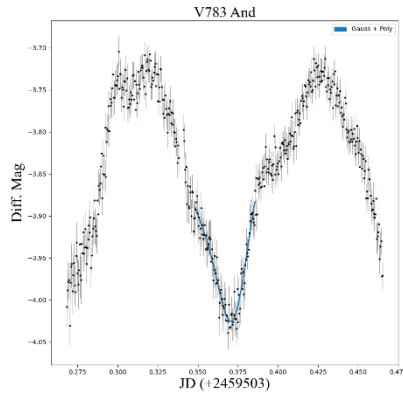
Şekil 1a, 1b, 2, 3 ve 4'de görüldüğü gibi elde edilen modellenmiş ışık eğrilerinden dört sistem için de minimum zamanları belirlendi.



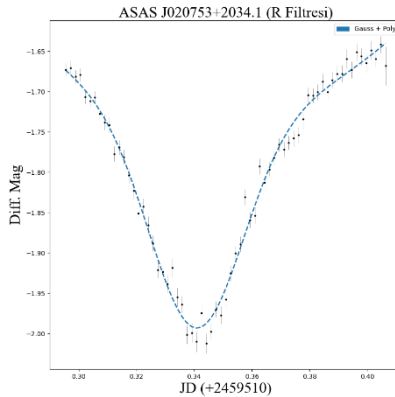
Şekil 1a. NSVS2175434 sisteminin R filtresi kullanılarak ATA50 teleskobu ile yapılan gözleminden elde edilen modellenmiş ışık eğrisi



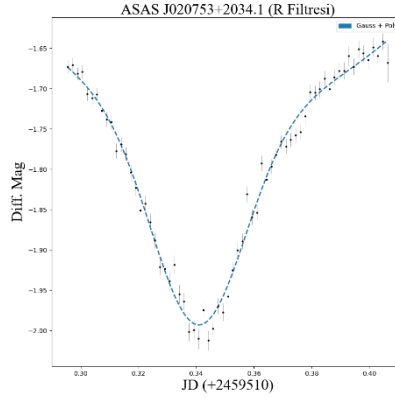
Şekil 1b. NSVS2175434 sisteminin B filtresi kullanılarak ATA50 teleskobu ile yapılan gözleminde elde edilen modellenmiş ışık eğrisi



Şekil 2. V783 And sisteminin R filtresi kullanılarak ATA50 teleskobu ile yapılan gözleminde elde edilen modellenmiş ışık eğrisi



Şekil 3. ASAS J020753+2034.1 sisteminin R filtresi kullanılarak ATA50 teleskobu ile yapılan gözleminde elde edilen modellenmiş ışık eğrisi



Şekil 4. NR Cam sisteminin R filtresi kullanılarak ATA50 teleskobu ile yapılan gözlemden elde edilen modellenmiş ışık eğrisi

Minimum zamanlar, JD (julian date)'den BJD (barycentric dynamical julian time)'ye dönüştürüldü [13]. Dört sistem için de türetilen minimum zamanları Tablo 2'de gösterildi.

Tablo 2 Dört W Uma sistemine ait elde edilen minimum zamanları

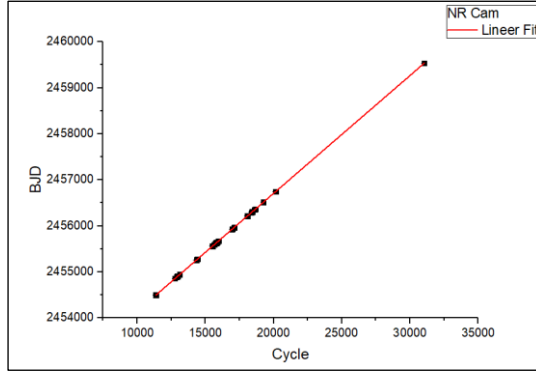
Kaynak	BJD	Hata
V783 And	2459503.37174581	0.0060
ASAS J020753+2034.1	2459510.34073458	0.0038
	2459510.33099462	0.0076
NSVS2175434	2459524.26392948	0.0026
	2459524.37377038	0.0027
	2459524.26353281	0.0036
	2459524.37320581	0.0038
NR Cam	2459535.26596463	0.0010
	2459535.39245006	0.0023

3. Yörünge Dönem Değişimi

Çift yıldız sistemlerinde görülen yörünge dönem değişimini inceleyebilmek için sistemlere ait literatürdeki minimum zamanlar araştırıldı. Ancak O-C diyagramını hazırlayabilmek için V783 And, ASAS J020753+2034.1 ve NSVS2175434 sistemlerine ait yeterli minimum zamanı bulunamadı. Bu nedenle sadece NR Cam için yörünge dönem değişimi incelendi. NR Cam sisteminin, Tavakkoli vd. (2015) tarafından verilen minimum zamanları ile yeni gözlemlerimizden elde edilen minimum zamanları birleştirildi [14]. İncelenen kaynağın yörüngesel dönemlerinde değişim olup olmadığına bakabilmek için her bir kaynağın elde edilen minimum zamanları Şekil 5'deki gibi lineer ışık elemanları ile fit edilir (Denklem 3).

$$BJD = T_0 + P_0L$$

Denklem 3

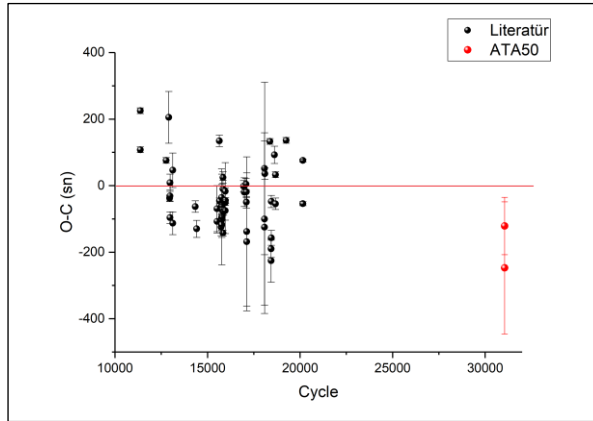


Şekil 5. Tüm minimum zamanlara uygulanan lineer efemeris modeli

Burada, T_0 doğruluğundan emin olunan başlangıç minimum zamanı, P_0 sistemin yörünge dönemi, L ise T_0 'dan itibaren meydana gelen örtülme sayısını temsil eder [15]. Tüm minimum zamanları ile Denklem 3 kullanılarak NR Cam sisteminin başlangıç minimum zamanı ve yörünge dönemi aşağıdaki gibi bulundu.

$$BJD = BJD\ 2451589.74618272(10) + L \times 0.2558861610(3)$$

Tüm minimum zamanları için elde ettiğimiz yeni başlangıç minimum zamanı ve yörünge dönemi ile sistemin O-C diyagramı Şekil 6'daki gibi elde edildi.



Şekil 6. NR Cam sisteminin O-C diyagramı

4. Tartışma ve Sonuçlar

Bu çalışma kapsamında NSVS2175434, V783 And, ASAS J020753+2034.1 ve NR CAM W Uma tipi dört örten çift yıldız sisteminin fotometrik gözlemleri yapılarak yörünge dönem değişimleri incelendi. İncelenen kaynaklardan NSVS2175434 sisteminin parlaklığı 13.6 kadir ve periyodu ise 0.221 gündür [16]. V783 And sistemi ise 13 Kasım 2013 tarihinde SuperWASP (Super Wide Angle Search for Planets) teleskobu ile keşfedildi ve 0.2090808 gün dönemli EW (W UMa) türü sistem olarak

sınıflandırıldı [17]. Diğer bir sistem olan ASAS J020753+2034.1 ise ASAS (All Sky Automated Survey) ile belirlenmiş olup parlaklığı yaklaşık 12.85 (V) kadirdir [18]. Son olarak NR Cam sistemi, Strohmeier (1958) tarafından başlangıçta 215 Cam olarak adlandırılan yavaş değişen bir yıldız olarak keşfedildi [14, 19]

Bu dört W Uma tipi örten çift yıldız sistemleri ATA50 teleskopu ile gözlemleri yapılarak dokuz yeni örtülme ışık eğrisi elde edildi. Bu ışık eğrileri gauss ve polinom fonksiyonlarının yer aldığı Gauss+Pol fonksiyonu ile fit edilerek dört kaynağa ait minimum zamanları elde edildi (Şekil 1, 2, 3 ve 4). Daha sonra O-C diyagramlarını oluşturabilmek için sistemlere ait literatürdeki minimum zamanları araştırıldı. NR Cam kaynağının dışındaki diğer üç kaynağın literatürde yeterli minimum zamanına sahip olmadığı için O-C diyagramı oluşturulamadı. Ancak, bu çalışma ile literatüre kazandırılan üç kaynağa ait minimum zamanları bundan sonra ki O-C çalışmaları için oldukça önemlidir.

Literatürde yeterli minimum zamanına sahip olan NR Cam için hesapladığımız başlangıç minimum zamanı ve sistemin yörünge dönemi Tavakkoli vd. (2015) tarafından verilenler ile uyumludur. Ancak Şekil 5'de de görüldüğü gibi NR Cam sisteminin O-C diyagramında net bir değişime rastlanmadı. Sonraki süreçte yörünge döneminde değişimin olup olmayacağını daha iyi anlayabilmek için daha uzun dönemli gözlem verilerine ihtiyaç duyulmaktadır

Teşekkür

Bu çalışmada, Atatürk Üniversitesi Astrofizik Araştırma ve Uygulama Merkezi (ATASAM) tarafından işletilen ATA50 teleskobu ve arkasındaki CCD kamera ile elde edilen veriler kullanılmıştır. ATA50 teleskobu Atatürk Üniversitesi (P. No. BAP-2010/40), CCD kamera ise Erciyes Üniversitesi (P. No. FBA-11-3283) Bilimsel Araştırma Projeleri Koordinatörlüğü Birimi (BAP) tarafından finanse edilmiştir. Gerekli verilerin toplanması için gözlem zamanı tahsis eden ATASAM yönetimi ve personeline teşekkür ederiz.

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ITO gas sensors for CO₂ and H₂ detection

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Abstract

Thin films with extensive characteristics and surface morphology are very important in designing high performance and reliable gas sensors. Therefore, comprehensive study carried out on ITO transparent conductive oxide resistive based H₂ and CO₂ gas sensors. As a result, bottom up prototype gas sensor device fabricated and tested in order to understand those properties and behaviors that effects on sensitivity. All the thin film deposited employing RF magnetron sputtering technique investigated by SEM, XRD, EDAX and Absorption methods. Different oxygen partial pressure introduced as a variable to optimize the surface thin film. Those synthesized material properties showed reasonable correlation with the sensitivities and response of ITO devices for reducing H₂ and CO₂ gases.

Key Words: Gas sensors, CO₂ sensor, H₂ sensor, RF sputtering, ITO

CCD ve CMOS Sensörlerin Çalışma Prensipleri ve Astronomi Alanındaki Yeri

Özet

Yüksek performanslı güvenilir gaz sensörlerinde ince filmlerin detaylı karakteritikle ve yüzey morfolojileri çok önemlidir. Bu nedenle şeffaf iletken oksit İTO direnç tabanlı H₂ ve CO₂ gaz sensörleri üzerinde kapsamlı bir çalışma yapılmıştır. Sonuç olarak, hassasiyete etki eden özellikleri ve davranışları anlamak için aşağıdan yukarıya prototip gaz sensör cihazı üretilmiş ve test edilmiştir. RF magnetron püskürtme tekniği kullanılarak biriktirilen tüm ince filmler SEM, XRD, EDAX ve Soğurma yöntemleri ile incelenmiştir. İnce filmlerin yüzey yapılarını optimize etmek için, değişken oksijen kısmi basıncı altında filmler büyütülmüştür. Sentezlenen bu

malzemelerin özellikleri, H₂ ve CO₂ gazlarını indirmek için ITO tabanlı gaz sensörü aygıtlarının duyarlılıkları ve tepkisi ile kabul edilebilir bir korelasyon gösterdi.

Anahtar Kelimeler: gaz sensör, H₂ sensör, ITO

1. Introduction

The gas sensors are requisite devices in regular life for detection odorless, hazards, toxic or explosive gases concerning public safety and environmental protection. Consequence of variety of technology and materials has been experimented to invent and explore best suited qualities of materials for improving characteristics of the sensors such as sensitivity, selectivity, and calibration stability, temperature [1,2]. Among those electronic noses, H₂ and CO₂ sensors started to flourish for their importance in variety of industries, transportation, environmental and health related fields. For instance, high pressure hydrogen gas becoming one of the most important alternative energy known as green energy with zero emission [1]. Thus hydrogen leak detection sensor technology became one of the priority concerns about reliability, safety, and economic reasons [2]. On the other hand, measurement and regulation of CO₂ gas is required in indoor spacing, agriculture field and bio-related processes [3]. Even though number of H₂ and CO₂ sensor exist, those are not sufficient when considering demand, simplicity and the cost perspective.

The indium tin oxide (ITO) wide optical band gap semiconductor thin films as a sensitive layer for gas detection investigated which widely applied as transparent conducting electrodes in flat-panel displays (FPD) [4], solar cells [5], and organic light emitting diodes (OLEDs) [6] due to their process dependency and highly degenerate electrical conductivity [8], high optical transparency [7]. ITO also can be considered as doped from In₂O₃ materials, known that very common material for gas detection[8]. Furthermore, ITO thin films with careful control of synthesis conditions can be achieved relatively low resistivity while maintaining high transparency that enhance the sensitivity of gas sensors.

Various growth conditions have an effect of increment in the carrier concentrations contributing to the widening of the bandgap, which is known as the Burstein– Moss shift. In addition to the carrier concentration, growth conditions strongly affect the crystallinity, impurity levels and surface roughness of the grown films. In this work, ITO thin film deposited employing RF-magnetron sputtering on soda lime glass substrate that method which characterized by high purity, low substrate temperature, good interfacial adhesion, high thickness uniformity and homogeneity [9]. The effect of O₂ partial pressure, on the structural, optical, and sensing properties of the ITO thin film deposited by RF-magnetron sputtering were successfully investigated. Furthermore, resistive based simple concept, low cost, repeatable, mass scale gas sensor device based on ITO thin film sensitive layer gas sensors fabricated. All thin film deposited on interdigitated electrodes (IDE) soda lime glass substrate operated at room temperature without post heat treatment. Moreover, structural and surface characterizations carried out by absorption techniques, x-ray diffraction (XRD) and field emission scanning electron microscope (FESEM). With help of analysis techniques remarkable transmittance and figure of merit observed. Importantly mechanism analysis were undertaken to study the correlation between the sensor performance and the materials structure. The gas-sensing

properties of the thin films were examined exposing the H₂ and CO₂ gas. The relationships between O₂ content and sensor performances were concluded. The influencing characteristics in the evaluation of the thin film also discussed. The gas sensitivity is explained by a change of the band bending on the surface of the metal oxides caused by adsorption of gas molecules. It is expected and proved that these prepared ITO thin films are promising for a H₂ and CO₂ gases.

2. Experiment

As illustrated in Figure 1, CO₂ and H₂ ITO sensors were fabricated through microfabrication process based on radio frequency (RF) magnetron sputtering system derived from 14 cm ITO metal target with high purity (ITO - 99.99%, 90% In₂O₃ and 10% SnO₂), in pure Ar and Ar/O₂ plasma. Indium tin oxide (ITO) thin films with a thickness of between 500nm-800nm deposited on soda lime glass (SLG) substrate and IDE patterned SLG substrate by reactive magnetron RF sputtering technique. The deposition optimized by changing O₂ partial pressure that has impact on crystallographic structure and opto-electrical properties of the films and on sputtering chamber conditions. The partial pressure of the oxygen in the chamber was varied up to 25% of growth pressures.

Standard cleaning procedure (ultrasonic bath of acetone, isopropyl, methanol and de-ionized water for 5 min.) followed to remove contaminants prior to deposition of ITO thin film and samples used in the device. The sensor fabrication was subjected to series of lithography process to fabricate all prototype sensors. As seen in the right side of the Figure 1, the lithography process was started with the photo resist coating by spin coating system under 5000 rpm condition for 50s followed by a soft bake at 110 °C. After exposure of UV light with the mask aligner SUSS Microtech MJB4, developing step was done for 5 min. The lithography process was finished by the hard bake at 120 °C for 2 min. All the sensors sensitivity measurement obtained by non-commercially available gas measuring system.

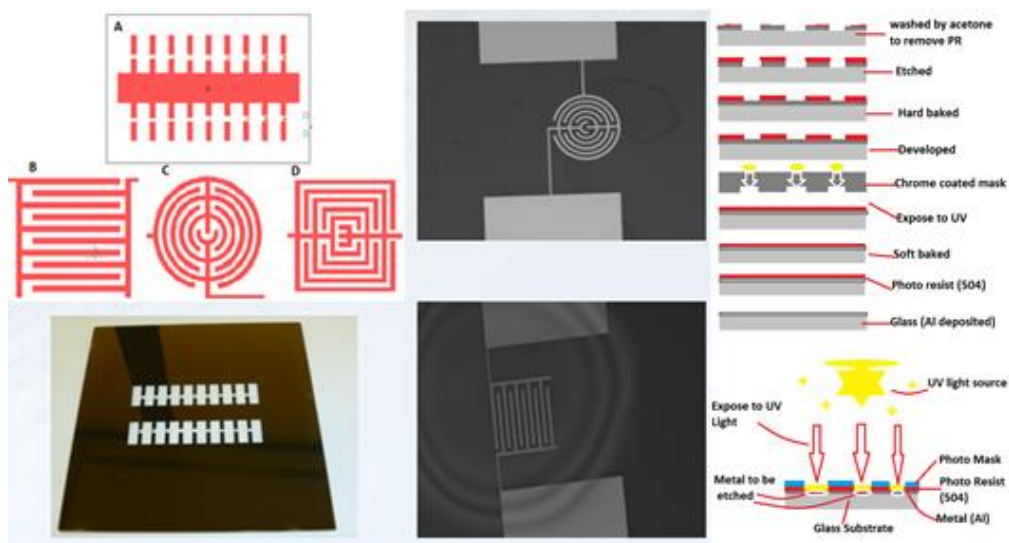


Figure 1. ITO thin film growth and sensor fabrication process.

The morphology characterization of the samples grown was performed with (FESEM) with Zeiss Sigma 300. The elemental analysis also was conducted with energy dispersive x-ray (EDX) detector attached to the FESEM system. The XRD measurements were made θ -2 θ condition between 10-90-degree PANalytical Emprayan XRD system.

3. Results and Discussion

From EDX composition analysis in Figure 2 a and the results in tabulated in Figure 2 b show that ITO film grown with ITO target deposited with pure Ar plasma with no oxygen gas contain zero Sn. This could be the result of that indium was formally evaporated because of its lower boiling point than Sn [10]. On the other hand, as the oxygen is included during the growth, the Sn composition appears in the EDX measurements (figures not shown). The Sn amount in ITO thin film is an important factor to

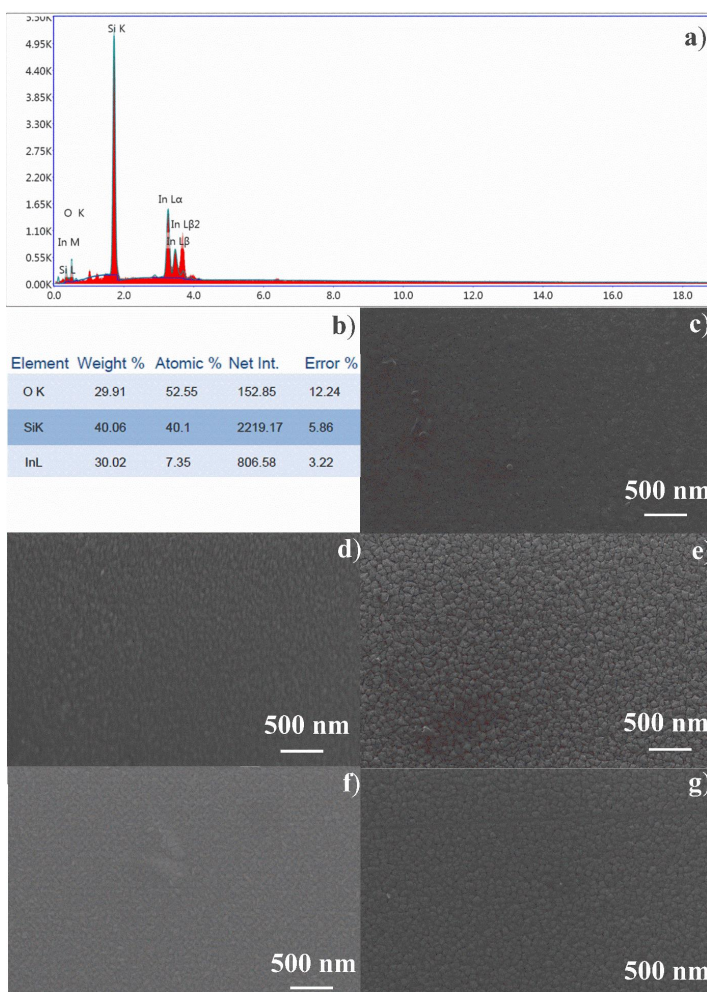


Figure 2. a) EDX data for the ITO grown under no oxygen pressure b) EDX element analysis c)-g) FESEM images of the ITO films of different oxygen partial pressure percentages to the total growth pressure 0%, 2.7%, 11.7%, 13.5%, 16.3%, respectively.

decrease the resistance of prepared ITO film [11], this no Sn contain sensor has shown the highest sensitivity. Figure 2 c-g have shown the FESEM images of the ITO thin films grown under different oxygen partial pressure percentages, 0%, 2.7%, 11.7%, 13.5%, 16.3%, respectively. It is shown that as the oxygen partial pressure percentage increases, the grain sizes observed in the FESEM images increase which is maximum for the 11.7% grown ITO film.

Figure 3 shows the XRD pattern of the sputtered ITO grains. The dominant peaks are indexed as (400) and (441) crystal faces of ITO which confirmed that the gains are polycrystalline. Increasing with the O2 content, the peak intensities belong to the ITO planes are increased as seen in the figure. Table 1 shows the calculated D values from the measured of the XRD data. The D values varies between 27 nm- 77 nm as seen in the table.

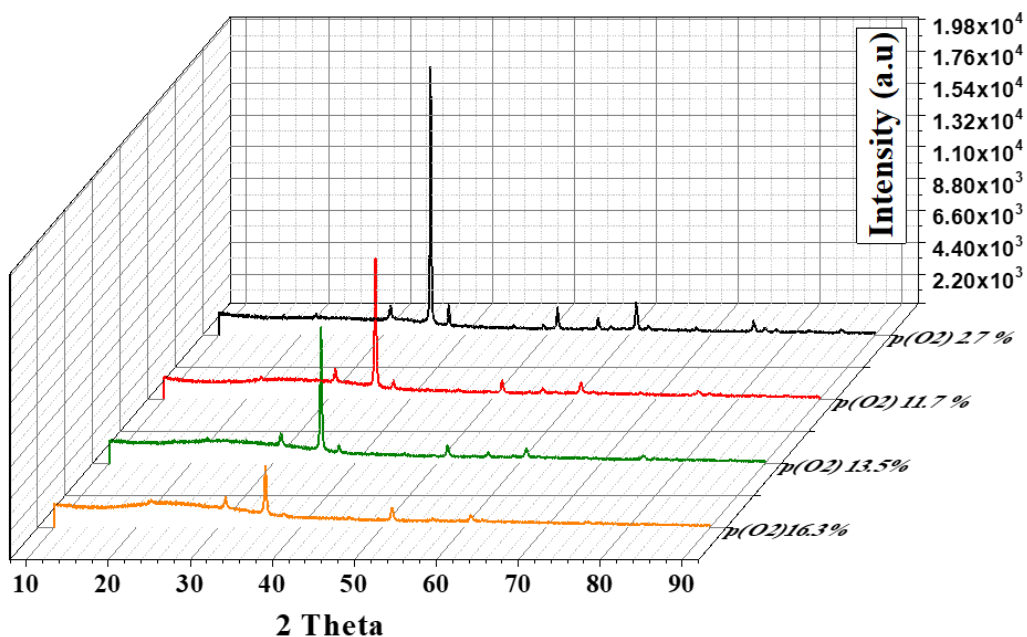


Figure 3. XRD figure of ITO films grown different O2 partial pressures

Table 1. Detail analysis of the XRD measurements

O ₂ %	Thickness (nm)	2θ (400)	I% (400)	FWHM (400)	D (nm)	2θ (441)	I% (441)	FWHM (441)
0	333	-	-	-	-	-	-	-
2.7	983	35.8	100	0.13	62.8	51.3	8.61	0.17
11.7	250	35.8	100	0.30	27.8	51.2	82.6	0.20
13.5	335	35.8	83.9	0.19	56.5	51.2	100	0.16
16.3	825	35.7	100	0.11	76.6	51.1	15.6	0.17
25	402	35.8	100	0.21	39.4	51.2	29.4	0.23

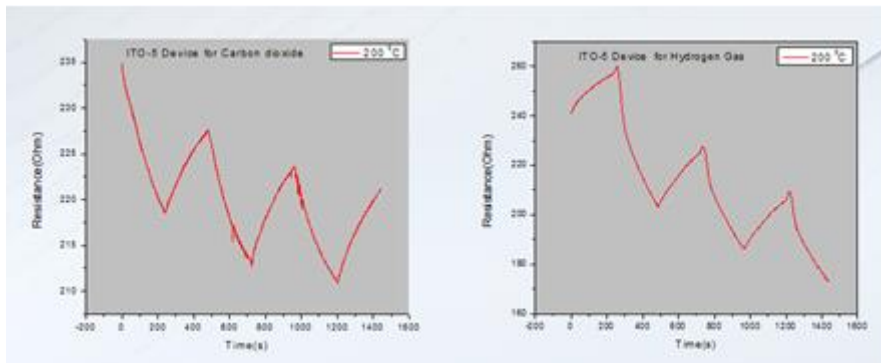


Figure 4. CO₂ and H₂ responses of the ITO sensor grown under 0% oxygen pressure.

Figure 4 shows a representative dynamic curve of the ITO sensor grown with no oxygen gas in the chamber. The concentration of CO₂ and H₂ for this test was 400 sccm. The optimal temperature to detect CO₂ and H₂ gases is at 200 °C which is plotted in Figure 4. The optimal working temperature is relatively lower than that of ITO thin film sensor which reported in other studies [7]. The resistance change, ΔR , of the sensors is monitored during sequential or periodic exposures to H₂ or CO₂. $\Delta R/R_0$ (sensitivity) is defined as the percent resistance change upon exposure to a gas with a fixed concentration of hydrogen and is calculated according to $\Delta R/R_0 = (R - R_0)/R_0$ where R_0 is the resistance of the sensor exposed to N₂ air and R is the maximum resistance after exposure to a gas containing hydrogen. Consequently, decreasing of the work function is beneficial to the flow of more electrons, resulted in decreasing of the resistance [12].

Good sensitivity (22%) of ITO sensor that contains no oxygen flow included during the growth could be related to the surface to volume ratio of nano-grains of the thin film. Table 2 and 3 have shown the responsivity, response and recovery time for some of the ITO sensors produced in the study. Recovery times for the CO₂ sensors are long. The reason for longer recovery time might be attributed that it took longer time for CO₂ desorbing from the nano-gains. A detail investigation expecting to carry out in future studies to find CO₂ adsorbing and desorbing by thin film. The fact that ITO nano grains have very large surface to-volume ratio which means a significant fraction of the atoms of ITO are surface atoms that can participate in surface reactions. This feature would contribute the resistance change of the ITO nano-grains, thus enhance the response the sensor and optimal working temperature. Another reason was related to the nature of the ITO surface, which was easy to react with H₂ because Sn doped material reported good sensitivity for H₂. Table 2 and Table 3 have shown the performances of the gas sensors characteristics.

Table 2. Responsivity, Response Time, Recovery time for H₂ at 200 °C

Responsivity			Response Time(S)			Recovery time(s)		
((R-R ₀)/R ₀)*100			(1-1/e)			(1/e)		
2.7%	25%	%0	2.7%	25%	%0	2.7%	25%	%0
10.9	9.8	22	32.8	23.6	92.3	36.4	4.4	24.2

Table 3. Responsivity, Response Time, Recovery time for CO₂ at 200 °C

Responsivity			Response Time(S)			Recovery time(s)		
((R-R ₀)/R ₀)*100			(1-1/e)			(1/e)		
2.7%	25%	%0	2.7%	25%	%0	2.7%	25%	%0
9.2	6.0	4.1	39.8	10.5	68.1	62.1	28.7	105.8

Semiconductor gas sensors are based on the conductivity changes of the semiconductor materials upon interaction with the target gas molecules. When the H₂ molecules were absorbed on the surface of the ITO nano-grains, electron transfer occurs between ITO and target gases. When the temperature was increased, the molecules were easier to react and be absorbed on the adsorption sites. However, desorption process existed at the same time. When the temperature was too high, the desorption process would become dominating which lowered the absorption of the gas. Consequently, there was an optimum working temperature for ITO nano-grain based sensor. A systematic investigation needed to prove further for CO₂. Besides the sensor response other parameters such as selectivity, response time and stability, are also very important. The testing for these parameters is in progress [13].

The dependence of the resistivity on the oxygen partial pressure is a well-known experimental result and is explained on the basis of oxygen deficiency in the film (each oxygen vacancy gives rise to two conduction electrons). Increasing oxygen content of the films by increasing the partial pressure of oxygen during the growth the samples in air or oxygen should decrease the oxygen vacancies leading to less conductive films. However, a minimum in the resistivity of the ITO thin films deposited on glass substrates is reported between 15 and 20% of oxygen partial pressure by a few investigators indicating an improvement in the crystallinity of the films (mobility of the carriers is dependent on crystallinity) [14].

4. Conclusion

ITO thin film has been successfully prepared by RF sputtering technique with the goals of improving sensitivity, simplicity and with RT temperature and without post heat treatment by enhancing performance of thin film controlling O₂ ratio for in H₂ and CO₂ sensing. The innovative sensing platforms demonstrated excellent sensitivity, response and recovery time. Device dependent sensitivities tested for range of operating temperature between of 30 °C – 200 °C. The distinct surface morphology and properties of ITO thin film with grain sizes play a key role improving sensitivity of

these sensors. The present result evidently proves that the methodology that applied to design ITO sensors could be one of the most promising TCO oxide-based gas sensors.

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Conflicts of interest

The authors declare that there are no potential conflicts of interest relevant to this article.

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Working Principles of CCD and CMOS Sensors and Their Place in Astronomy

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Abstract

In this article, information about the properties, working principles and recent developments of CCD and CMOS sensors used in astronomy are given. Until the development of camera technology, sky observations were made using photographic plates in telescopes. With the development of CCD sensors in the 1960s, photographic plates were replaced by powerful cameras with CCD and CMOS sensors. Even today, all observations made in the optical field are made with the data taken by placing these cameras in the ocular part of the telescope. It is of great importance to understand the sensor technology in order to understand the observation techniques. This article has been prepared to fill this gap.

Key Words: Astronomy, Telescope, Sensor, CCD, CMOS.

CCD ve CMOS Sensörlerin Çalışma Prensipleri ve Astronomi Alanındaki Yeri

Özet

Kamera teknolojisinin gelişmesine kadar, teleskoplarda fotoğraf plakaları kullanılarak gökyüzü gözlemleri yapılmıştır. 1960'larda CCD sensörlerinin geliştirilmesiyle, fotoğraf plakalarının yerini CCD ve CMOS sensörlü güçlü kameralar aldı. Bugün bile optik alanda yapılan tüm gözlemler, bu kameraların teleskoplara monte edilerek alınan verilerle yapılmaktadır. Gözlem tekniklerini anlamak için sensör teknolojisini anlamak büyük önem taşımaktadır. Bu makalede CCD ve CMOS sensörlerin özellikleri, çalışma prensipleri ve son gelişmeler hakkında bilgi verilmiş ve sensör teknolojisinin astronomide kullanımı incelenmiştir.

Anahtar Kelimeler: Astronomi, Teleskop, Sensör, CCD, CMOS.

1. Introduction

Photosensitive digital cells are called sensors or optical sensors. CCD and CMOS sensor technology are used today in camera systems, cameras of mobile phones, digital cameras and many systems that are sensitive to image creation. As a result of the demand for these systems, sensor technology is gaining momentum day by day.

The sensors convert the incoming optical image into electronic signals. They consist of light-sensitive cells called photodiodes on sensors. Photodiodes receive light and convert photons into electrical signals. The resolution/pixel of the sensor is proportional to the number of photodiodes. For example, 10 megapixels means 10 million photodiodes. The higher the resolution, the higher the detail quality. If the sensor is produced in small sizes, the photodiodes will be smaller and accordingly less light will be received. Thus, it is understood that sensors with high pixels do not always have high quality. Light sensitivity needs to be increased in order to both use small photodiodes and improve image quality [1].

It is important in terms of image quality that the sensors used in astronomy are produced in large sizes. However, due to the widespread use of mobile products and being more commercial/economical products, small-sized sensors are produced more [2]. Especially silicon sensor technology is used in the field of astronomy. Due to the need for large focal planes in astronomy, large CCD sets have been produced. Newly produced CCD and CMOS sensors are designed with low noise and high measurement accuracy. This feature is also important for obtaining accurate data in astronomical observations [1,3].

2. Material and Methods

2.1. Fundamentals of Sensor Technology

Sensors are devices or subsystems that detect events/information in their environment and send them to other electronic devices (processors). The sensors are used compactly with other electronic devices. In addition to numerous applications, it is also used in everyday objects such as lamps that darken or brighten when touched. With the development of micro-devices and simple-to-use microcontrollers, the use of sensors has moved beyond the very general pressure, humidity or flow measurements. Sensors are generally designed to have little effect on what is being measured. Reducing the size of the sensor often makes it better and provides convenience. Technological developments have opened the door to the production of more sensors at microscopic scale with micro sensors using MEMS technology. Oftentimes, a micro-sensor provides a very fast and short measurement time and higher precision results compared to large systems. Today, the demand for fast, economical and reliable information has increased. Thus, the importance of disposable sensors has increased recently. Using them, important analytical data can be easily obtained by anyone without any problems [1].

There are two basic types of sensors used in almost all digital camera/measurement systems. One of them is CCD (Charge Coupled Device) sensor and the other is CMOS (Complementary Metal Oxide Semiconductor) sensor. CMOS sensors are divided into two main groups as passive pixel sensors and

active pixel sensors. There is also a type of sensor that can capture three colors in a single pixel [4]. We will discuss on CCD and CMOS in this article.

2.2. CCD (Charge Coupled Device)

CCD (Charge Coupled Device) sensors, which were discovered by Willard Boyle and George Smith in 1969, have been developed with the advancement of technology and have come to the present day. The working logic of the CCD sensor is to capture the photons coming from the light source. These captured photons form photoelectrons. The resulting photoelectrons are collected in cells called photocells. These electrons formed in the cells are counted and stored together with their coordinates [4].

There are versions of CCD sensors produced and put into use in different ways. One of them, One Chip-One Shot technology, has three basic color-sensitive filters, RGB (Red-Green-Blue) on the sensor. In this way, basic color separation is done on the CCD. CCDs produced by this method are mostly used in entry-level products. It has relatively low costs. In addition to the Two-Chip method RGB filter, there is also a second sensor for brightness. Another method is One Chip-Three Shot technology. In this, after the light falling on the sensor is divided into three parts, RGB, it is exposed with a special filter. Regardless of the technology, CCD sensors are expensive to manufacture, require more energy than other sensors, and require a large area for use. Therefore, CCD sensors are not generally preferred in mobile phones. CCD sensors are more preferred in fields such as special astronomy, as they give relatively higher quality and clear images [5].

2.2.1. Working Principle of CCD

CCDs are based on Metal Oxide Semiconductor (MOS) capacitors technology. Embedded channel capacitors are used for manufacturing. A thin n-type embedded channel is formed by ion doping on the surface of a p-type substrate. A silicon dioxide insulator layer is formed over the n-region and metal or heavily doped polycrystalline silicon gates are placed on top of the CVD (chemical vapor deposition) insulated SiO₂ to fill the capacitor. The main material of CCDs is mostly silicon semiconductors. These sensors are extremely sensitive to light. Capturing photons from the light source, a CCD cell performs four tasks: It takes the charge from the cell above the layer, holds the charge for a while, transfers this charge to the cell below the layer, and produces its own energy. It charges by reacting to external factors such as light [1].

Rays from the light source form photoelectrons. The resulting photoelectrons are collected in the cells in photocells. These electrons formed in cells are counted and stored together with their coordinates. CCD sensors, whose raw material is usually silicon semiconductors, have a light sensitive structure. They convert light into electronic signals and are sent to image processors for processing with this sensitivity. The signals processed on the image processor are converted into digital signals and stored on memory cards [1][4].

The speed, sensitivity, resolution, and cost of a CCD sensor affect its performance. Which CCD type to choose depends on the areas where the devices will be used. Frame transfer structure is used in

astronomy because maximum light must be captured. However, the most used in cameras is the interline transfer structure. The three structures used to apply the value read from the CCD array can be described as follows:

- i. Full Frame:* The entire CCD array acts as the active area. Charges pass through vertical CCDs in parallel and are then removed in series from horizontal CCDs, using a shutter mechanism to block light from reaching the elements. This process takes a lot of time.
- ii. Frame Transfer:* Half of the adjacent array area is used for exposure and the remaining half is opaque. Loads are transferred from the active region to the opaque region in a short time and are read from there. This operation is faster than full frame reading. However, it has a disadvantage that it uses twice the silicon area.
- iii. Interline Transfer:* Each pixel has an active area and an adjacent opaque area. Charges are quickly transferred from the photosensitive photodiode to the adjacent vertical CCD unit. There is also the disadvantage of increasing silicon area here. However, with modern developments, it is possible to increase the quantum efficiency of the array by using micro lenses that direct the light away from the opaque regions [7]

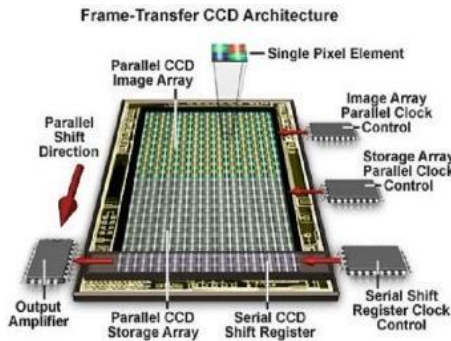


Figure 1. Frame Transfer CCD Architecture [6].

The sensitivity of a CCD device is usually a function of its operating temperature. As the temperature increases, the leakage light-free current also increases, thus decreasing the sensitivity. In devices with a CCD sensor, Signal Noise Ratio (SNR) degradation may occur due to photon noise, readout noise, or a combination of these. CCD arrays are only sensitive to density, not color. Filters are used to obtain color images. Color images can be obtained using a Bayer filter or a 3CCD and dichroic beam splitting prism [8].

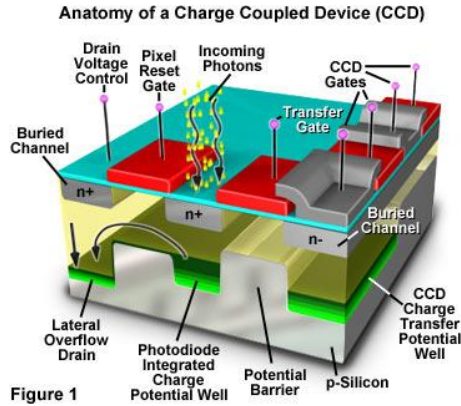


Figure 2. Anatomy of a CCD [6].

2.3. CMOS (Complementary Metal Oxide Semiconductor)

CMOS sensors were discovered by Frank Wanlass in 1963. Like CCDs, they convert light into electronic signals. These sensors consist of hundreds of transistors. Each pixel is generated by a separate transistor. CMOS sensors are widely used. The reason for this is that they have been widely used in devices other than cameras for years and show a continuous development [10],

With this widespread use, CMOS sensors, which can be produced at affordable prices, are often preferred especially in entry-level digital cameras. Especially small floor coverings are one of the most important reasons for this. It is a product frequently encountered in mobile phones, tablets, compact machines and DSLR devices. In addition, factors such as low energy need and not taking up much space play an important role in the preference of these sensors [10,11].

2.3.1. Working Principle of CMOS

CMOS sensors, just like CCD sensors, work according to the photoelectric effect system to convert light into electricity. All CCDs and CMOS sensors perform the same basic tasks: charge generation and collection (light to charge conversion), measurement and conversion to voltage or current, finally signal output.

CCD sensors move the photographic charge from pixel to pixel and convert it to voltage at an output node, as shown in the diagram below; CMOS imagers instantly convert the charge inside each pixel to voltage. Modern CMOS sensors also contain an amplifier for each pixel. After amplification, the voltage output of the pixel is transferred over a micro wire at the output of the chip [11].

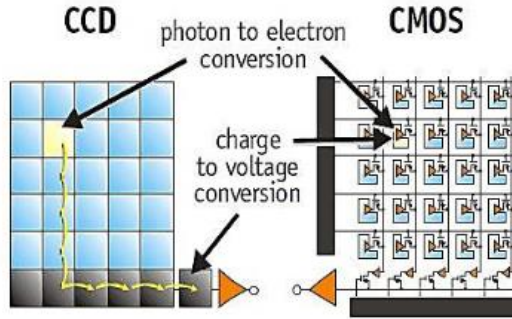


Figure 3. Working differences of CMOS and CCD [11].

2.4. Differences Between CCD and CMOS

Since CMOS sensors do not take up much space, they are preferred especially in small devices (such as mobile phones, tablets). CMOS sensors can operate with less energy. This means longer battery life. Because CMOS sensor technology is used in many devices, it is inexpensive and easy to manufacture.

CCD sensors generally operate with much lower noise than CMOS sensors. The light sensitivity of CCDs is much higher than that of the CMOS sensor. Therefore, although CMOS gives successful results in bright environments, they give worse results in low light conditions than CCD sensors. CCD sensors produce low noise and high quality images. However, CMOS sensors catch up with the technology and approach CCD technology in terms of quality [12].

3. The Place of CCD and CMOS Sensors in Astronomy

Image quality and low noise are very important in astronomy, as small arcsecond fields are precisely observed. The sensors that meet these conditions have always been CCDs. Although CMOS sensors have been used in astronomy in recent years, CCD use is older and more common.

The use of CCD cameras in astronomy is one of the best detectors we have with current technology, although the CCD chip is not an optically ideal detector. Therefore, it is a detector mostly used in telescopes. External factors such as sensor readout noise, thermal noises, and cosmic rays can alter pixels in the CCD array. So to counter such effects, astronomers take several exposures with the CCD shutter closed and open so that the CCD-acquired images can be analyzed. The average of images (Bias) taken with the shutter closed is required to reduce noise. After the Dark Frame average image is taken, it is subtracted from the light shutter image to clear dark current and other structural defects (dead pixels, hot pixels, etc.) in the CCD. For these processes, images (Bias, Dark, Flat) specific to each CCD are calibrated [12].

3.1. Historical Process and Importance

From the 1900s to the present, there have been great developments in astronomical instruments with telescopes. Telescopes with larger mirror diameters have been produced. Since there are no CCD detectors to record the observation data, photographic images are obtained by using photographic plates (glasses coated with silver halide) placed on the focal plane of the telescope. In addition, the glass wedge placed in the focal plane of the Telescope is adjusted until the intensity of the star is equal to the light intensity of a preselected standard star, and the images taken are calibrated by comparing this glass wedge, and in photographic photometry the brighter the star image on a plate, the larger the star size. Some instruments such as micrometers and thermocouples are used with these photographic plates. In addition, the blink microscopes used for comparison were used to distinguish the differences in the plates by rapidly rotating the plates taken at different times. Although CCDs came into our lives in the 1970s, these methods were used until the end of the 1900s and CCDs replaced photographic plates in astronomy [13].

CCDs were first produced at Bell Laboratories in the 1970s. The first CCD 1969 Willard Boyle and George Smith single array 8 pixel detector. Later, in 1973, the Jet Propulsion Laboratory (JPL), NASA and TI jointly started a large-area CCD development program for Astronomy. The first commercial CCD device was produced by Fairchild in 1974. In 1974, the Moon was imaged using an 8 inch Telescope with a Fairchild CCD (100x100 pixels), and this is the first astronomical CCD image. Among the earliest astronomical applications of a CCD for ground observation were made at the University of Arizona in 1976 (Smith 1976). The first CCD-based reconnaissance satellite, KH-11 KENNAN, was launched in 1976. CCD development continued over the years, and in 1979 Radio Corporation of America (RCA) developed a liquid nitrogen-cooled CCD system [14].

Continuing developments from the 1980s to the present have led to devices with over 100 million pixels, read noise as low as an electron, quantum efficiency close to 100%, and useful sensitivity close to X-rays to IR. While CCDs have fallen out of favor with CMOS imagers for commercial imaging applications, they are still cutting-edge sensors for astronomical imaging due to their size, efficiency and low noise. Over the years, scientists who make astronomical instruments have developed CCDs specific to their areas of interest [1,14].

In 1983, CCDs began to replace photographic plates in astronomical telescopes. Kodak produced CCD-based professional cameras until affordable, high-resolution cameras began to hit the market in 1995 [1].

3.2. Basic Definitions

There are special requirements for astronomical imaging, astronomers have often made special CCD sensors for their own observing needs. These special requirements are:

Pixel Size: Larger than normal pixels are used in astronomy due to sensors, large full well capacity and dynamic range.

Dark Current: Exposures taken with the CCD's diaphragm closed. The electron flow resulting from the heating of the CCD and electronic parts is called black current. The exposure time for Dark is given

as much as the exposure time of the object to be observed. eg. If we are going to observe the Polaris star with exposures of 20 seconds, images are taken with an exposure time of 20 seconds for the dark.

Quantum Efficiency: It is the ratio of the number of photons measured to the number of all incoming photons. If this value is 1, it means that all incoming photons are captured by the detector, and there is no such perfect instrument. An instrument with a quantum efficiency of 90% is considered sensitive.

Bias: It is the exposure taken in zero seconds while the aperture is closed. Returns the electronic noise value in the CCD [12]. Raw Biased Frames are created with zero light to the camera. Science frames are created that take zero-second exposures (shortest exposure) in the same grouping mode (1x1, 2x2). After creating a Master Bias, it can be used until the ambient temperature is too high to regulate the CCD temperature anymore or a change is made to the electronic path of the system.

Dark: The thermal movements of electrons within the chip produce signals gradually, proportional to the exposure time, not because they are exposed to optical light, but because these thermal electrons have a chance to accumulate in each pixel over time. The Dark Frame is made to measure the "dark current" or thermal signal in the CCD chip so that it can be extracted from the data images.

Flat: Not every pixel in the CCD has the same sensitivity. The middle pixels are brighter and the edges are dimmer. These are images taken to correct for different distribution. The exposure time is given as half the saturation level of the pixels. In which filter the object to be observed will be observed, flat is taken in the same filter [12].

4. New Developments

CCD and CMOS sensors have made great advances in recent years. Low noise ratio, high resolution and quality images are provided. CMOS sensors, on the other hand, have caught up with CCD sensors at a better viewing point, although they are made in smaller sizes.

Thinned CMOS sensors have been produced for use in astronomy. Examples of these are TAOS-II CIS113 sensor, NGSD/LGSD CIS112 sensor, CIS115 sensors. For large space programs, sensor technologies such as GAIA CCD91, Euclid CCD273, Plato CCD270, Rosetta have been developed. Studies are also underway on EMCCD and Red Sensitive CCDs [2, 16].

5. Conclusion

What makes a digital camera digital is the image sensor in the camera. That is, an image sensor converts the light captured by the camera's lens into a digital signal. This digitized light is processed and stored in the camera's memory as a digital file that you can view on the computer later. Next to the lens, the image sensor is the key element that ensures quality video. There are two main types of camera image sensors: CCD and CMOS. Both types of image sensor technologies contain hundreds of thousands or even millions of pixels. We can think of a pixel as a small bucket that captures light and converts it into an electrical signal. CCD and CMOS sensors have different advantages, but technology is evolving rapidly and the situation is constantly changing. Therefore, the best strategy for a camera manufacturer is to constantly evaluate and test the sensors for each camera. The field of astronomy

is also an area that can no longer progress without sensor technology. With each passing day, we will see that more powerful sensors are produced.

Conflicts of Interest

The authors declare that there are no potential conflicts of interest relevant to this article.

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