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Electrocatalytic Oxidation of Ethanol and Bioethanol Using Poly(thionine) Supported Platinum Nano/Micro Particles

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Abstract

Pt micro/nano particles were supported on poly(thionine) conducting polymer and used as catalyst for electrochemical oxidation of ethanol. Thionine was polymerized from its aqueous solution by cyclic voltammetry. Incorporation of Pt complex was carried out electrochemically by polycyclic voltammetry using K_2PtCl_4 as the precursor prior to reduction. Evaluation of optimum experimental parameters was done according to the obtained oxidation currents recorded in ethanol solutions with cyclic voltammetry. For the physical characterization of the Pt/PTH catalyst prepared under optimum conditions, SEM images were recorded. When the cyclic voltammetric behavior of bioethanol with the Pt/PTH catalyst prepared under optimum conditions was examined and compared with synthetic ethanol, it was revealed that the developed catalyst showed high catalytic activity for bioethanol oxidation.

Keywords: poly(thionine), platinum, ethanol, bioethanol, electrocatalysis

Poli(tiyonin) Destekli Platin Nano/Mikro Partikülleri Kullanılarak Etanolün ve Biyoetanolün Elektrokatalitik Yükseltgenmesi

Öz

Pt mikro/nano parçacıkları poli(tiyonin) iletken polimer destek malzemesi üzerinde sentezlenmiş ve etanolün elektrokimyasal yükseltgenmesi için kullanılmıştır. Tiyonin, sulu çözeltiden dönüşümlü voltametri ile polimerleştirildi. Pt kompleksinin polimer film yapısına immobilize edilmesi, sulu K_2PtCl_4 çözeltisinden dönüşümlü voltametrik taramalar ve ardından kimyasal veya elektrokimyasal indirgeme yoluyla gerçekleştirildi. Deneysel parametreler, etanol çözeltisinde kaydedilen pik akımı değerlerine göre optimize edildi. Optimum şartlarda hazırlanan Pt/PTH katalizörünün fiziksel karakterizasyonu için SEM görüntüleri kaydedildi. Optimum şartlarda hazırlanan Pt/PTH katalizörü ile biyoetanolün dönüşümlü voltametrik davranışı incelenip sentetik etanol ile karşılaştırıldığında geliştirilen katalizörün biyoetanol yükseltgenmesi için yüksek katalitik aktivite gösterdiği ortaya çıktı.

Anahtar Kelimeler: poli(tiyonin), platin, etanol, biyoetanol, elektrokataliz

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Introduction

In today's world, as the energy need is continuously rising and the existing energy resources are decreasing, energy-related research has recently been focused on renewable energy sources. Fuel cells, one of the class of devices that use renewable energy sources depending on the type of fuel, have a significant potential as environmentally friendly systems. Today, polymer electrolyte membrane (PEM) fuel cells are accepted as devices that can replace existing batteries, especially in portable devices. The most preferred fuel cells are systems that use H2 or methanol as fuel. However, there are still some problems in this system. A fuel cell simply consists of an anode, a cathode and the electrolyte membrane that separates these two parts, which can be described as the heart of the fuel cell. In general, fuel is fed to the fuel cell from the anode, while the oxidant is fed from the cathode. Electrocatalytic reactions occur on both sides, so the surface area of the electrodes, especially the anode is of critical importance for performance (Saleh & Easton 2013).

In the design of a fuel cell, selection of the electrode material is crucial with the purpose of increasing the efficiency as well as reduction of the cost of a fuel cell system. The materials used for the construction of the catalyst layers contain a metallic catalyst material (often Pt in PEMFCs) which are usually combined with a suitable supporting platform. Pt containing catalyst materials are generally advantageous for the design of anodes as well as cathodes while less expensive non-precious metals may be used for the construction of the cathode compartment (Sönmez Çelebi, 2016).

There are many factors that are important for the efficiency of a noble metal particle-based catalyst, such as particle size and dispersion, the methods used for preparation, supporting environments, etc. The electrocatalytic activity of an electrode material can be easily improved by incorporation of a conducting polymer as the supporting medium for immobilization of the metal nanoparticles (Huang et.al., 2009; Mohanraju et.al., 2015; Sönmez Çelebi et. al., 2008; Sönmez Çelebi & Pekmez 2017; Sönmez Çelebi et. al., 2020). As described by Kralik and Biffis (Kralik &Biffis 2001), there are three steps during the preparation of metal particles supported on functional polymers: synthesis of the polymer support material, decoration of the polymer from a convenient metal particle precursor, and generation of the metal particles within the polymer.

Among the alcohol-based fuel cells, methanol is the most common fuel owing to its advantages such as low cost, ease of handling and transportation. However, it also has some disadvantages such as being a toxic substance with one of the highest ecotoxicity scores (Bai et. al., 2019). Ethanol is an alternative for methanol because it is quite attractive as a fuel as a renewable energy source. Ethanol, which is referred to as bioethanol, can be obtained in large quantities via fermentation of some agricultural products such as sugarcane, wheat, corn, etc. (Badwal et.al., 2015). Platinum-either alone or as a bimetallic catalyst- supported on a conductive support material such as a suitable C-based material or a conducting polymer is commonly used as an electrocatalyst for oxidation of ethanol at the anode of an ethanol fuel cell (Singh and Mahapatra 2023; Vigier et.al. 2004; Zhang et.al. 2023; Zhou et.al. 2003).

Herein, we describe the preparation of Pt micro/nano particle-based catalyst using poly(thionine) (PTH) conductive polymer as the support material and to test its effectiveness for the electrocatalytic oxidation of ethanol. Optimization of the experimental conditions for the preparation of the catalyst was carried out according to the oxidation peak currents obtained from the cyclic voltammetry (CV) experiments recorded in ethanol solution in acidic medium. Characterization of the PTH supported catalysts prepared under optimum conditions was further performed by electrochemical and physical methods, namely CV and Scanning Electron Microscopy (SEM).

Materials and Methods

We obtained thionine monomer, H_2SO_4, K_2PtCl_4 and ethanol from Sigma-Aldrich and used without further purification. 80% hydrazine hydrate solution in water was obtained from Merck and used after dilution. The dissolved oxygen existed in the solutions were removed by bubbling 99.99%

nitrogen gas through the cells. No temperature adjustment was needed, the electrochemical experiments were all done at ambient temperature. A CHI 600E electrochemical workstation connected to a personal computer was used with a three-electrode system glass cell. The working electrode was a Tombow pencil connected graphite electrode, PGE, with a geometrical area of 6.48 x 10^{-2} cm^2. All potentials were recorded using a silver/silver chloride reference electrode (Ag/AgCl) and a linear platinum (Pt) wire was the auxiliary electrode. Scanning electron microscopy (SEM) images were recorded using JEOL model JSM-7001F.

Results and Discussion

Modification of the Electrode

The modification process includes three consecutive steps: *i)* electropolimerization of thionine onto the electrode surface, *ii)* immobilization of Pt complex ions into the polymer matrix, *iii)* reduction of the complex to obtain Pt nano/micro particles. To determine the optimum experimental conditions and to test the activity of the catalyst for ethanol oxidation, cyclic voltammograms of 0.5 M ethanol solution containing 0.5 M H_2SO_4 were recorded, and peak current values were compared.

Determination of Optimum Polymer Film Thickness

Deposition of the PTH film was carried out electrochemically with polycyclic voltammetry on the surface of the PGE from 0.05 M thionine monomer solution which also contained 0.5 M H_2SO_4 to serve as supporting electrolyte. The potential limits were -0.2 V and +0.8 V vs. Ag/AgCl in the negative and positive region (Figure 1a). Comparison of the cyclic voltammograms of the blank solution recorded with the uncoated PGE and PTH coated PGE clearly indicates the polymer coating (Figure 1b).

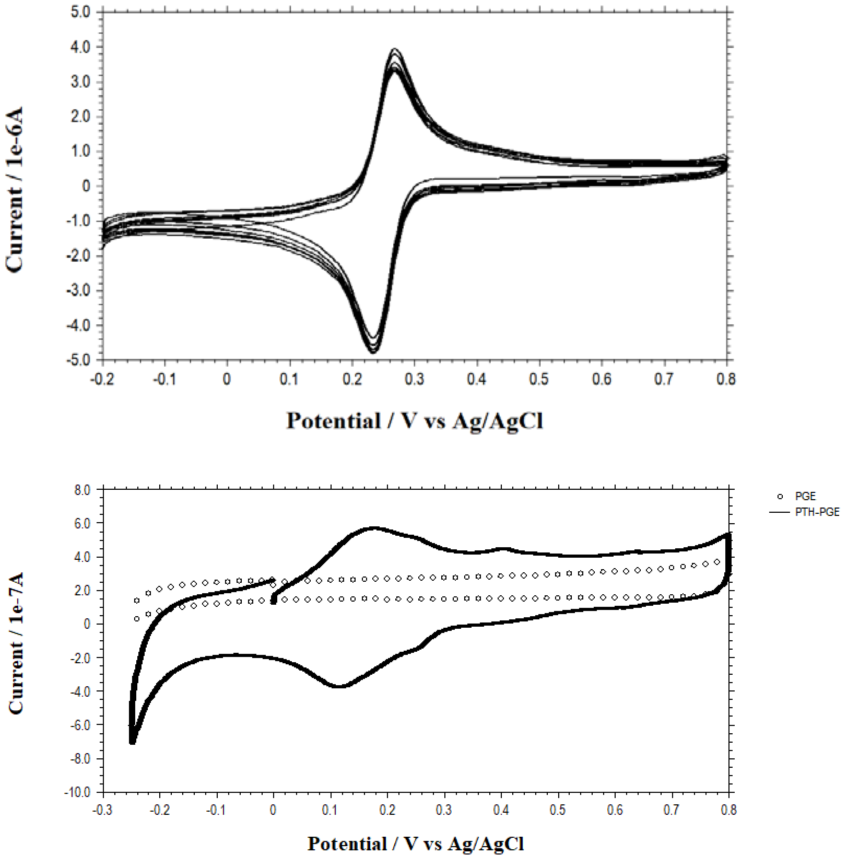


Figure 1. a) Polymerization of Thionine from 0.5 M Monomer Solution b) Cyclic Voltammograms Recorded in 0.5 M H_2SO_4 with Uncoated PGE (ooo) and PTH Coated PGE (—) (Scan rate: 0.1 V s^{-1})

Determining the appropriate polymer film thickness was important to obtain the best supporting medium for Pt particles. Polymer film was coated onto the electrode surface using 5, 10 or 15 cycles, and then a fixed amount of Pt was introduced into the resulting polymeric film and subjected to chemical reduction. When the ethanol voltammograms recorded with Pt/PTH catalysts prepared with polymer films of different thicknesses were compared, it was observed that the maximum peak current was observed with the catalyst obtained using 10 cycles (Figure 2).

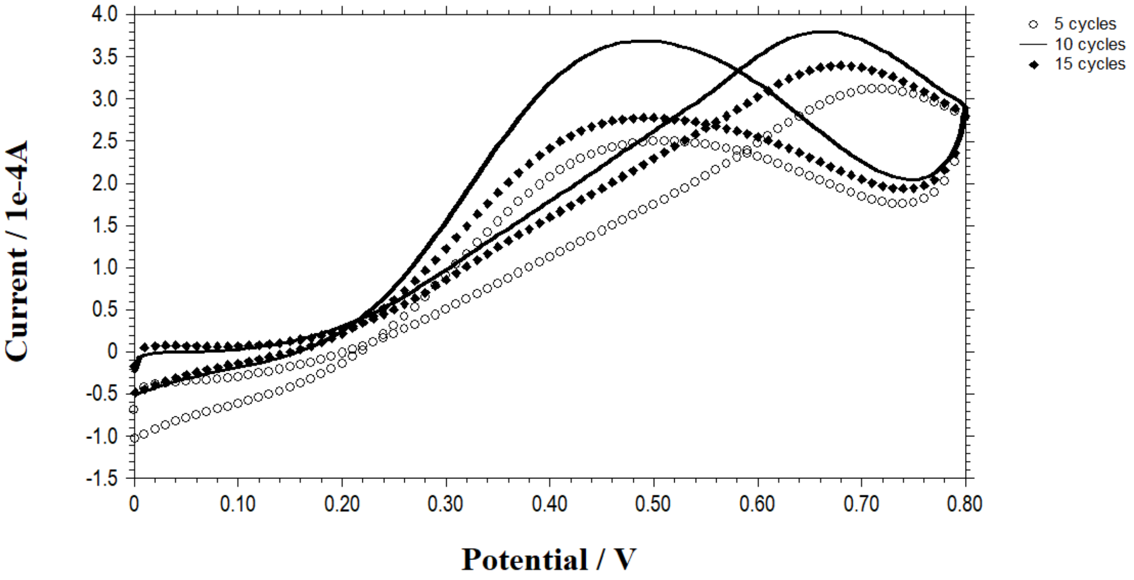


Figure 2. Cyclic Voltammograms of 0.5 M Ethanol Solution Recorded with Pt/PTH Modified PGE Prepared with Polymer Film of Different Thicknesses (Scan rate: 0.100 V s^{-1})

Immobilization of Pt Complex into the Polymer Matrix

One of the most important steps during the preparation of the catalyst is the immobilization of Pt particles into the polymer film. At this stage, when the PTH-coated electrode is immersed in a 2 mM K_2PtCl_4 solution without a supporting electrolyte and cyclic voltammetry was performed, the $PtCl_4^{2-}$ complex is immobilized into the polymer matrix in each cycle, and then the metal particles can be obtained on the electrode surface by chemical or electrochemical reduction. An example polycyclic voltammogram is presented in Figure 3a. In Figure 3b, the influence of the Pt loading is given according to the ethanol voltammograms recorded with various amounts of Pt controlled by the number of cycles in Pt precursor. As seen from the voltammograms, maximum peak current for ethanol oxidation is obtained for 60 cycles of Pt loading.

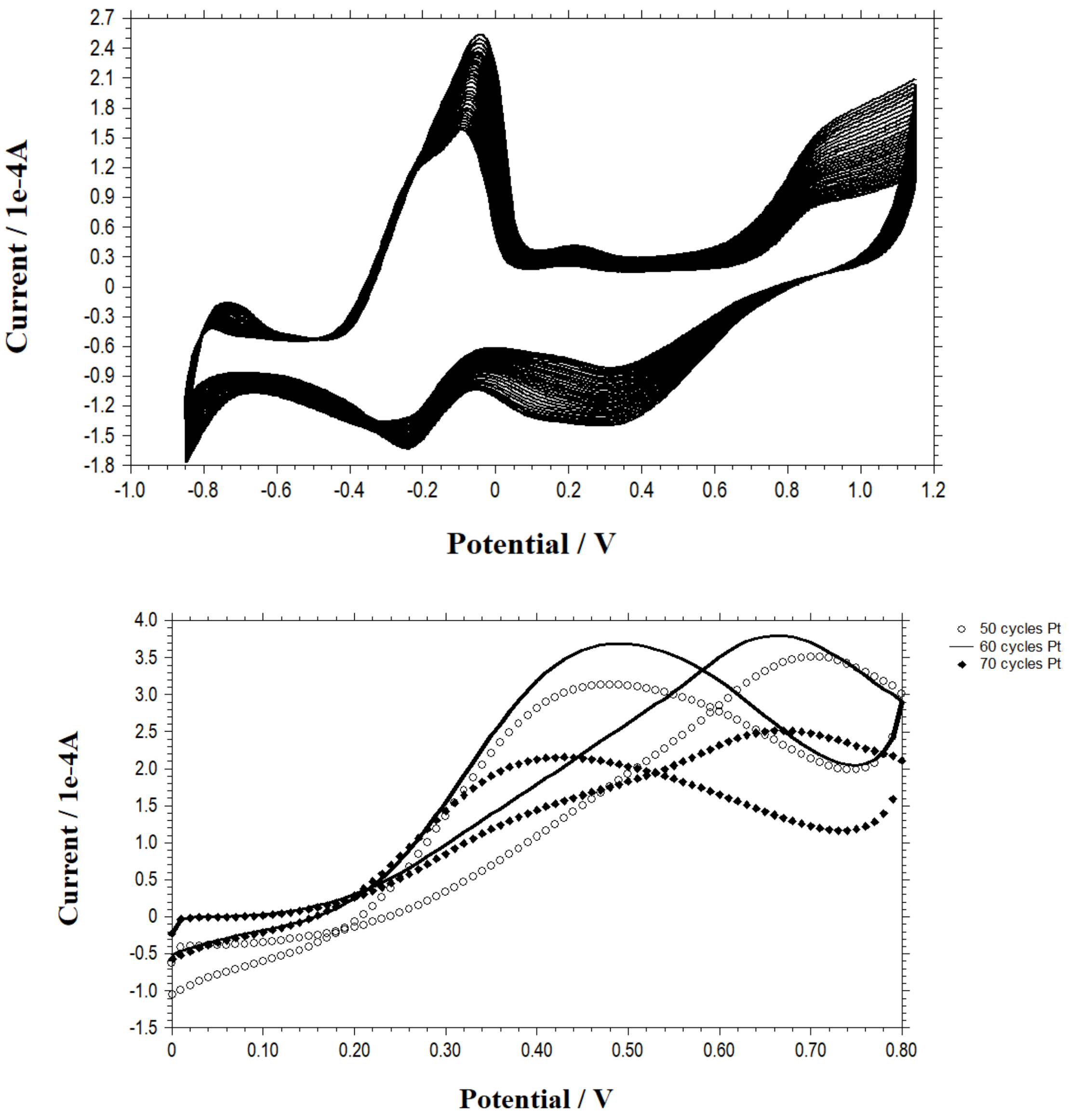


Figure 3. a) Polycyclic Voltammogram Rrecorded with PTH-coated PGE in 2 mM K_2PtCl_4 solution b) Cyclic Voltammograms of 0.5 M Ethanol Solution Recorded with Pt/PTH Modified PGE Containing Different Amounts of Pt Particles (Scan rate: 0.1 V s^{-1})

Reduction of the Pt Complex

After the immobilization of the Pt complex ions, an appropriate reduction process must be applied to convert it to its metallic form. For this purpose, chemical and electrochemical reduction methods were compared. We first studied chemical reduction by immersing the $PtCl_4^{2-}$ containing polymer film 0.1 M hydrazine solution which was stirred continuously. When the cyclic voltammograms of the ethanol solution were recorded with the catalyst systems obtained by reducing for 30, 60 and 90 minutes, it the best result was achieved with a reduction of 60 minutes and this condition was accepted as the optimum chemical reduction time.

For the electrochemical reduction, electrolysis was performed by applying a -0.2 V potential in 0.5 M H_2SO_4 solution, and ethanol voltammograms recorded with the catalysts obtained using different electrolysis times were compared. Electrolysis times of 5, 10, 15 and 20 minutes were studied, and the best result was obtained with the catalyst electrolyzed for 10 minutes.

In order to test which reduction method is better, the chemical and electrochemical reduction methods were compared by recording ethanol voltammograms (Figure 4).

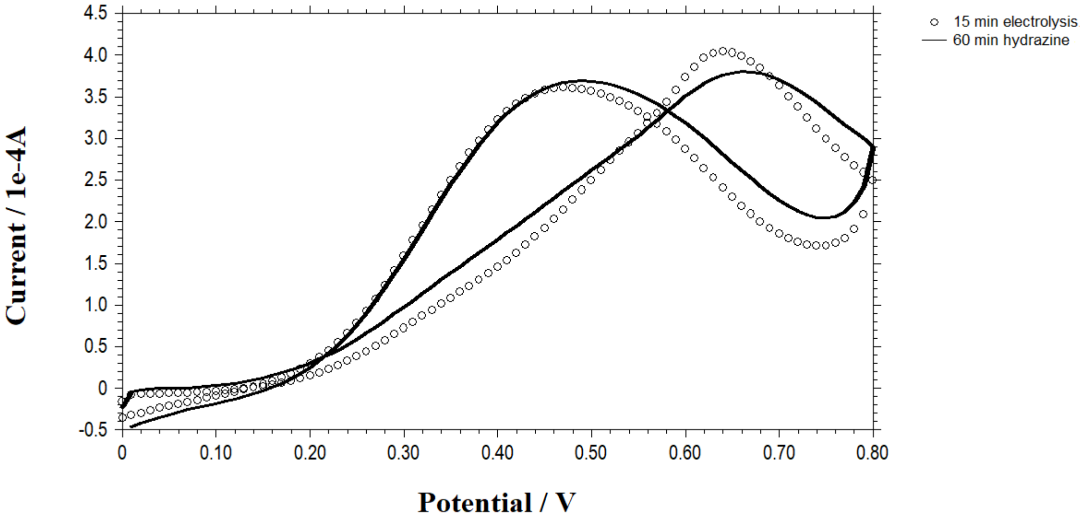


Figure 4. Cyclic Voltammograms Recorded with Pt/PTH Modified PGE Prepared by Chemical and Electrochemical Reduction Methods in 0.5 M Ethanol Solution (Scan rate: 0.100 V s^{-1})

By means of oxidation peak current, the two reduction methods gave very similar results. Therefore, to further investigate the better reduction method, we compared cyclic voltammograms recorded in H_2SO_4 (Figure 5a) and ferri/ferro solutions (Figure 5b). According to both hydrogen adsorption/desorption peaks and ferri/ferro couple redox behaviors, chemical reduction method appears to be better for reduction of the Pt complexes.

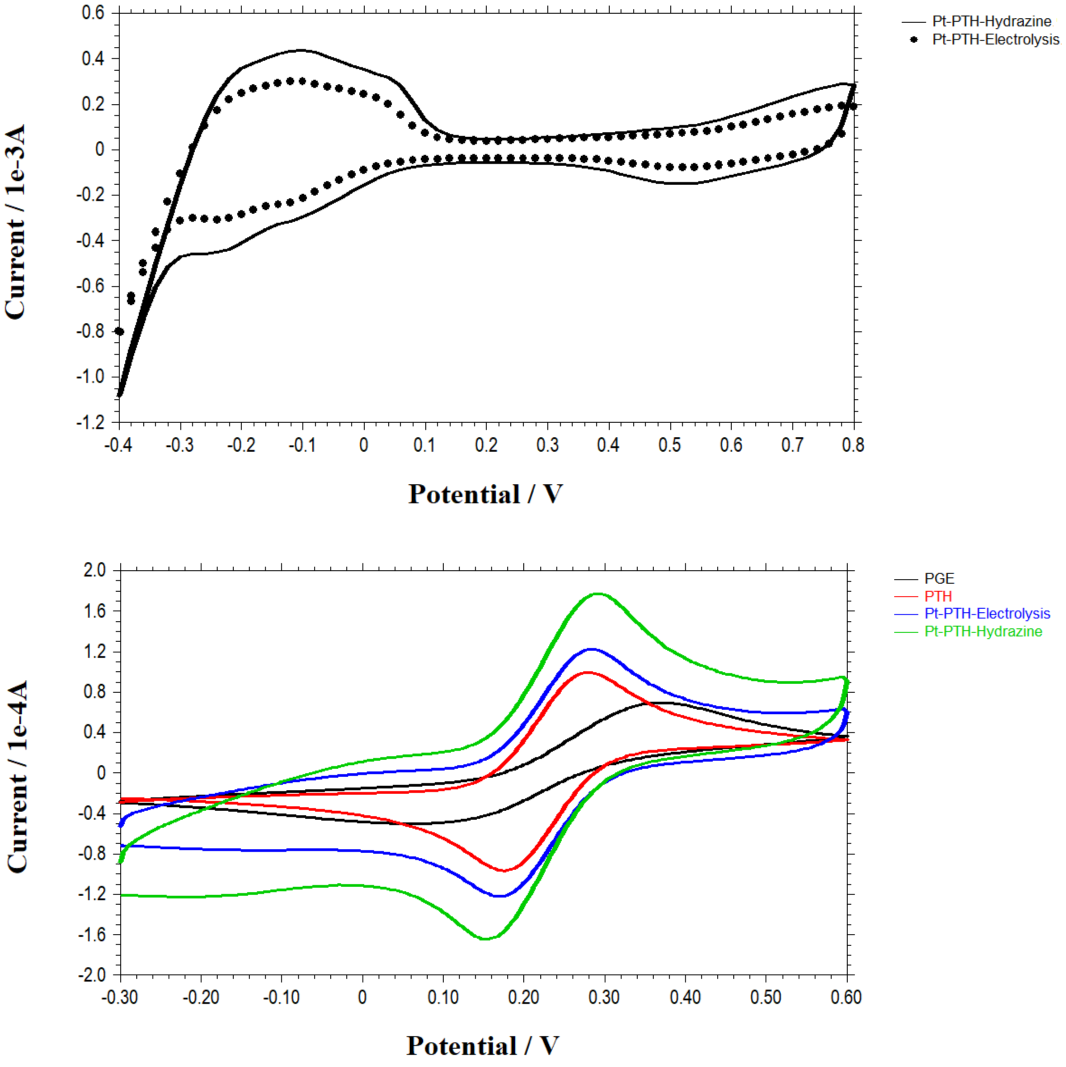


Figure 5. Cyclic Voltammograms of a) 0.5 M H_2SO_4 solution b) 5 mM $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ Redox Couple Recorded with Catalysts Prepared by Chemical and Electrochemical Reduction (Scan rate: 0.1 V s^{-1})

Scanning Electron Microscopy (SEM) Characterization

SEM images of the catalysts were recorded for the physical characterization of the Pt/PTH catalysts prepared by both reduction methods. Figures 6-9 show the SEM images recorded for naked PGE, PTH-coated PGE, Pt/PTH-coated PGE prepared by electrochemical reduction and Pt/PTH-coated PGE prepared by chemical reduction, respectively. When the images are examined, it is understood that both the polymer and Pt particles are properly coated and finely dispersed on the electrode surface, and a coating with a porous structure as desired is obtained.

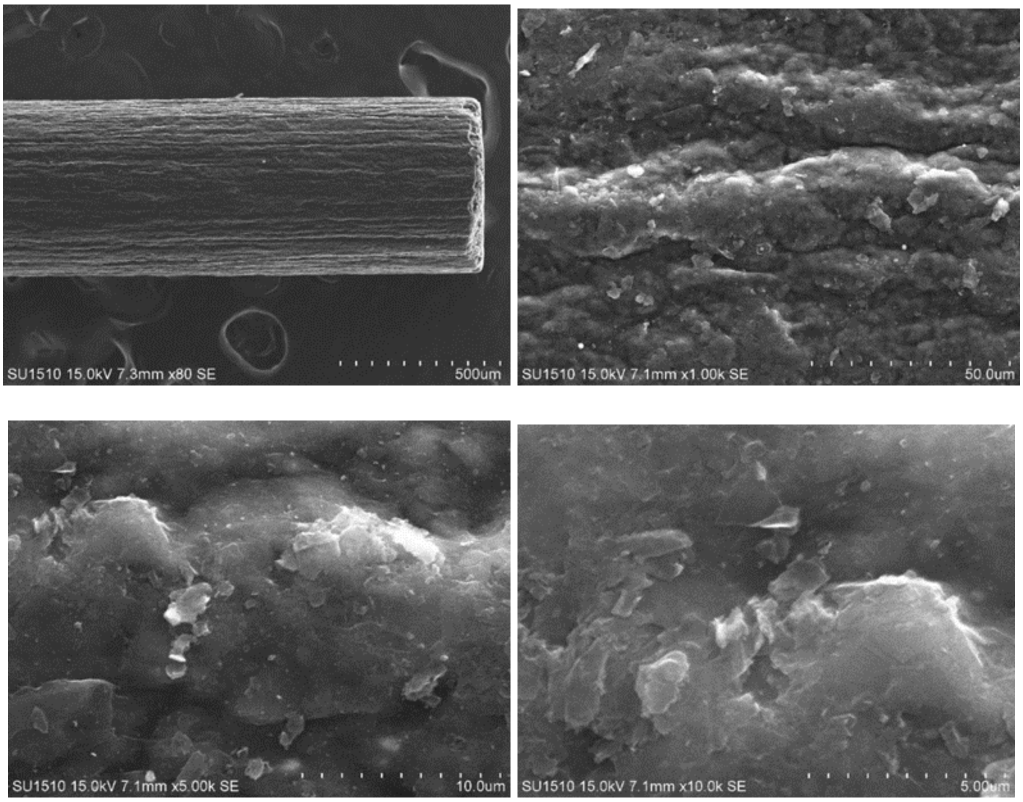
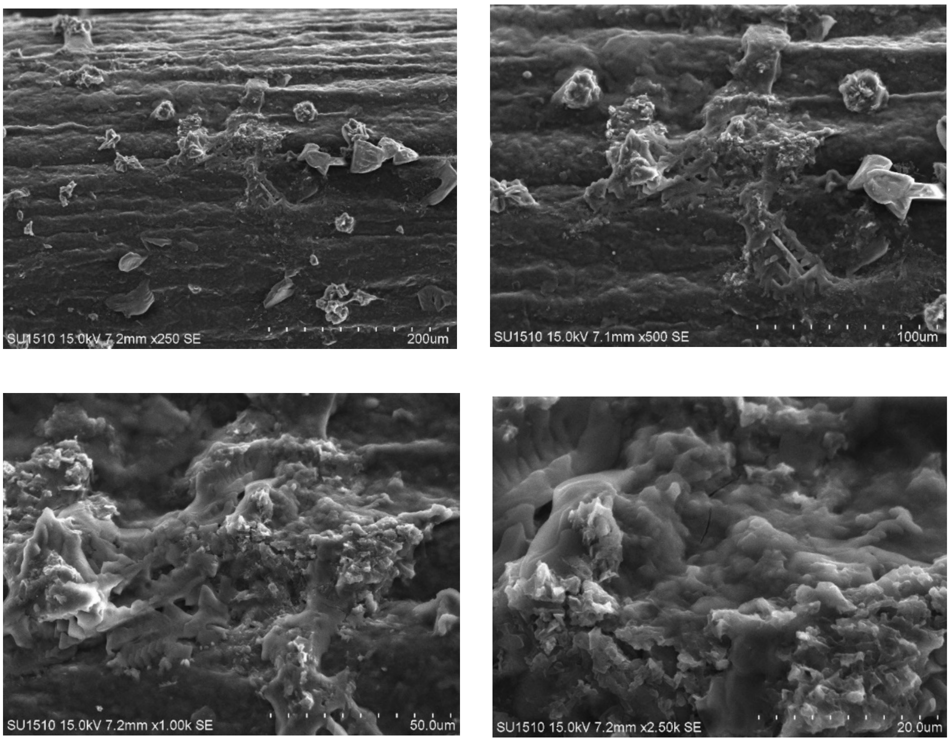


Figure 6. SEM Images Recorded with Uncoated PGE at Different Magnifications



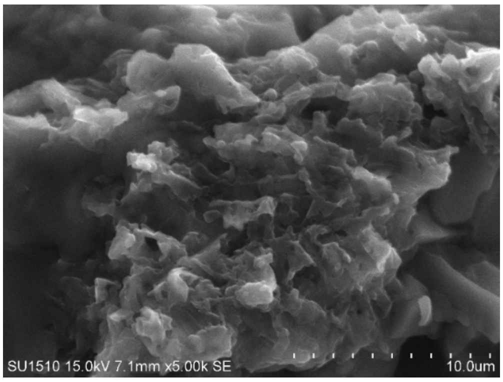
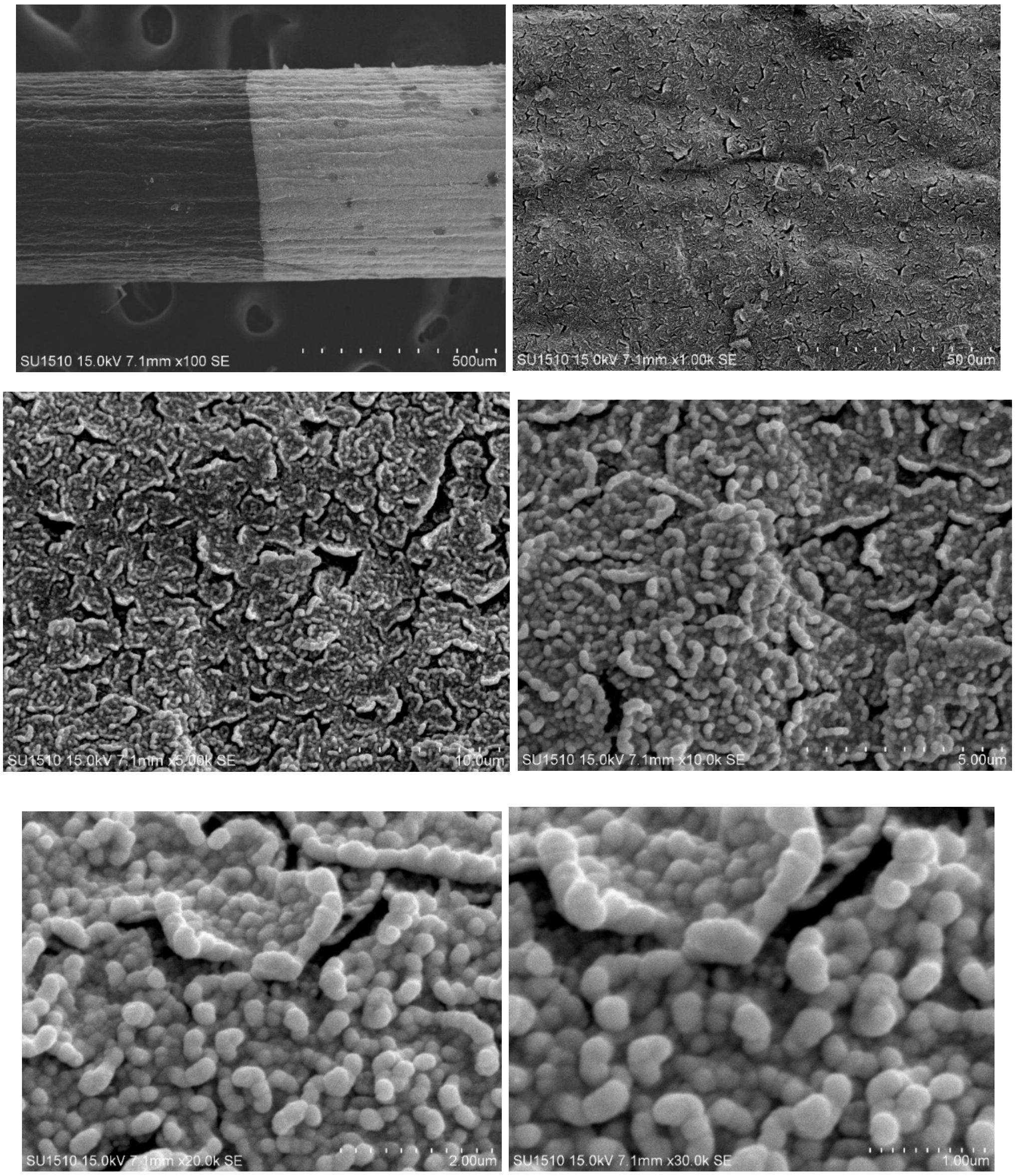


Figure 7. SEM Images Recorded with PTH-Coated PGE at Different Magnifications



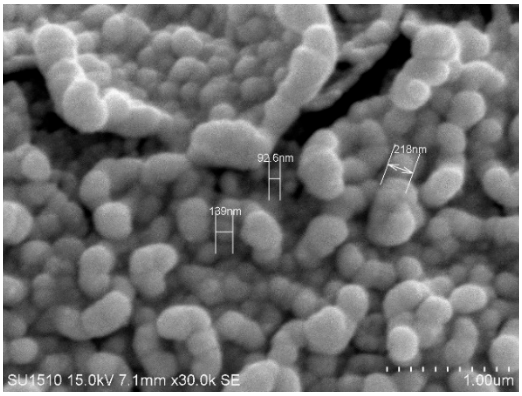
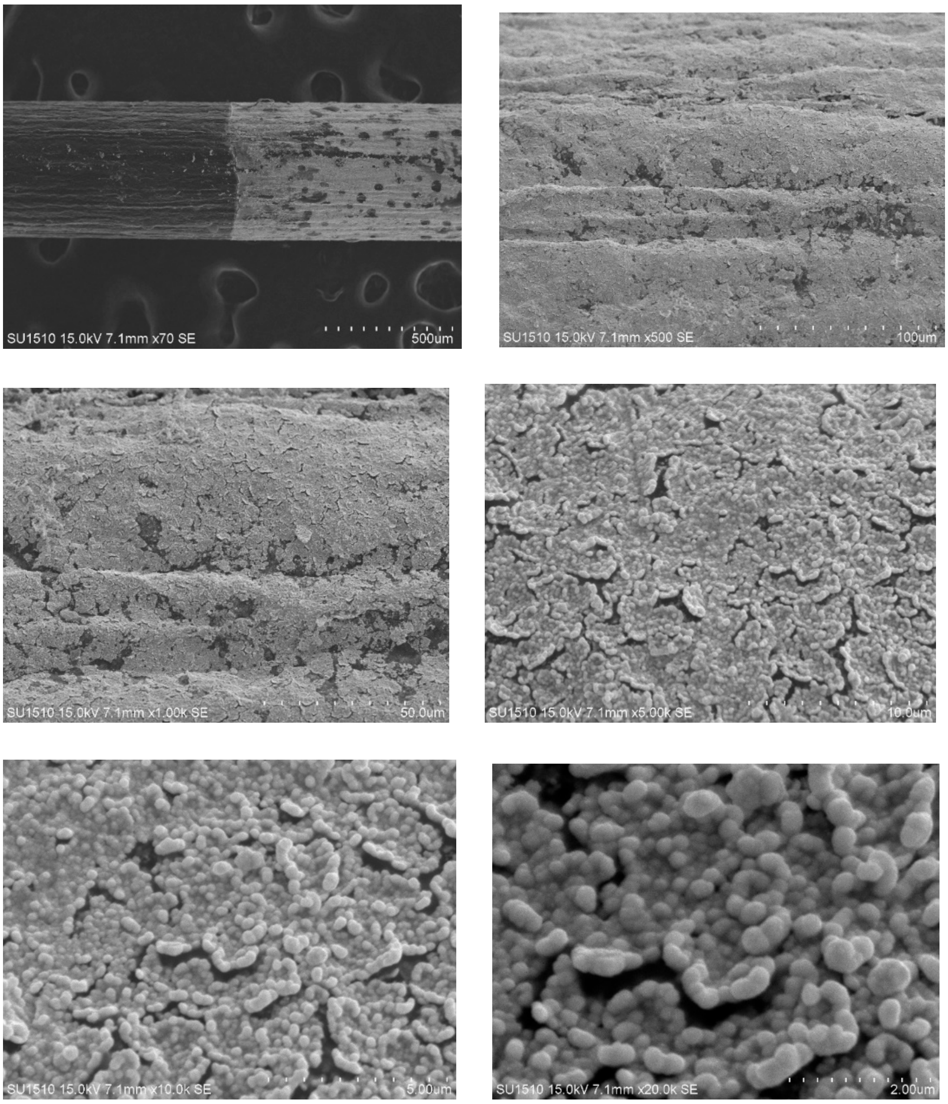


Figure8. SEM Images Recorded at Different Magnifications with Pt/PTH Catalyst Prepared by Electrochemical Reduction



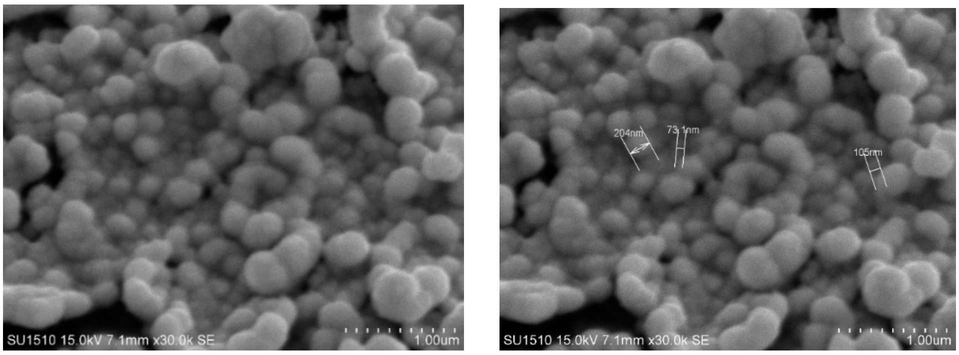


Figure9. SEM Images Recorded at Different Magnifications with Pt/PTH Catalyst Prepared by Chemical Reduction.

Bioethanol Oxidation with Pt/PTH Catalyst

The ultimate goal of the study is to develop an effective catalyst for the electrocatalytic oxidation of bioethanol obtained from plants as a renewable energy source. For this reason, it is very important for the Pt/PTH catalyst system to show high catalytic activity against bioethanol. In Figure 10, the cyclic voltammograms of bioethanol and synthetic ethanol recorded with the Pt/PTH catalyst are compared. As can be clearly seen from the figure, when bioethanol was used, a higher current and advantageous potential was observed compared to synthetic ethanol in terms of both peak current and peak potentials. Therefore, it is obvious that the Pt/PTH catalyst developed in this study shows high catalytic activity for bioethanol oxidation.

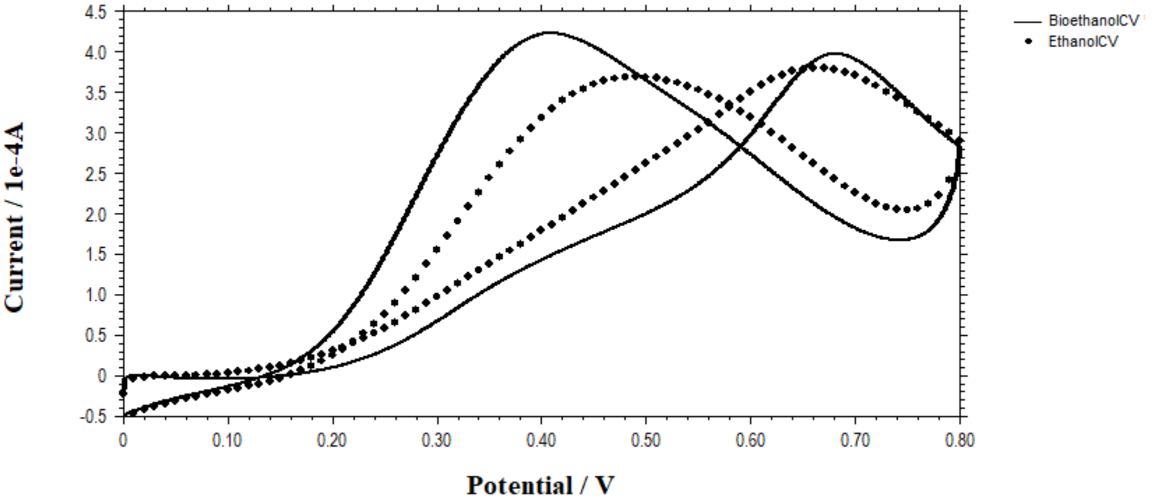


Figure 10. Cyclic Voltammograms of 0.5 M Bioethanol (—) and Synthetic Ethanol (●●●) Solutions Recorded with Pt/PTH Coated PGE (Scan rate: 0.100 V s^{-1})

Conclusions

PTH supported Pt micro/nano particles were prepared for the electrochemical oxidation of bioethanol, a renewable energy source. In order to optimize the experimental conditions, the oxidation peak currents obtained from the CVs recorded in ethanol solution were compared. The Pt/PTH catalyst was physically characterized by recording SEM images. When the cyclic voltammetric behavior of bioethanol with the Pt/PTH catalyst system was examined and compared with synthetic ethanol, it was revealed that the developed catalyst showed high catalytic activity for bioethanol oxidation.

Acknowledgment

The study was produced from the master's thesis titled "Electrocatalytic Oxidation of Bioethanol Using Poly(Thionine) Supported Platinum and Palladium Nanoparticles" which was carried out by Nuriye Şahin under the supervision of Mutlu Sönmez Çelebi (Thesis no. 864965).

Author Contribution

Nuriye Şahin, conducted the experiments, collected, and analyzed the results. *Mutlu Sönmez Çelebi*, supervised experiments and data collection and was responsible from all stages of manuscript preparation.

Ethic

There are no ethical issues with the publication of this article.

Conflict of Interest

The authors state that there is no conflict of interest.

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References

Badwal, S. P. S., Giddey, S., Kulkarni, A., Goel, J., & Basu, S. (2015). Direct ethanol fuel cells for transport and stationary applications–A comprehensive review. *Applied Energy, 145,* 80-103. https://doi.org/10.1016/j.apenergy.2015.02.002

Bai, J., Liu, D., Yang, J., &Chen, Y. (2019). Nanocatalysts for electrocatalytic oxidation of ethanol. *ChemSusChem, 12(10),* 2117-2132. https://doi.org/10.1002/cssc.201803063

Huang, S. Y., Ganesan, P., & Popov, B. N. (2009). Development of conducting polypyrrole as corrosion-resistant catalyst support for polymer electrolyte membrane fuel cell (PEMFC) application. *Applied Catalysis B: Environmental, 93(1-2),* 75-81. https://doi.org/10.1016/j.apcatb.2009.09.014

Kralik, M., & Biffis, A. (2001). Catalysis by metal nanoparticles supported on functional organic polymers. *Journal of Molecular Catalysis A: Chemical, 177(1),* 113-138. https://doi.org/10.1016/S1381-1169(01)00313-2

Mohanraju, K., Sreejith, V., Ananth, R., & Cindrella, L. (2015). Enhanced electrocatalytic activity of PANI and CoFe2O4/PANI composite supported on graphene for fuel cell applications. *Journal of Power Sources, 284,* 383-391. https://doi.org/10.1016/j.jpowsour.2015.03.025

Saleh, F. S., & Easton E. B. (2013). Determining electrochemically active surface area in PEM fuel cell electrodes with electrochemical impedance spectroscopy and its application to catalyst durability. *Electrochimica Acta, 114,* 278-284. https://doi.org/10.1016/j.electacta.2013.10.050

Singh, B. K., & Mahapatra, S. S. (2023). Performance study of palladium modified platinum anode in direct ethanol fuel cells: A green power source. *Journal of the Indian Chemical Society, 100*(2), 100876. https://doi.org/10.1016/j.jics.2022.100876

Sönmez Çelebi, M., Pekmez, K., Özyörük, H., & Yıldız, A. (2008). Preparation and physical/electrochemical characterization of Pt/poly (vinylferrocenium) electrocatalyst for methanol oxidation. *Journal of power sources, 183*(1), 8-13. https://doi.org/10.1016/j.jpowsour.2008.05.010

Sönmez Çelebi, M. (2016). Energy applications: Fuel cells. A. Tiwari, F. Kuralay, and L. Uzun (Ed.), *Advanced electrode materials* (397-434) içinde. Wiley-VCH.

Sönmez Çelebi, M., & Pekmez, K. (2017). Electrooxidation of formic acid using Pt nanoparticles supported on conducting poly vinylferrocene polymer support. *Hacettepe Journal of Biology and Chemistry, 45(3)*, 351-358. https://dergipark.org.tr/en/pub/hjbc/issue/61905/926356

Sönmez Çelebi, M., Kırlak Kara, S., & Çoşkun Kurt, N. (2020). Electrocatalytic oxidation of formic acid using Pt nanocatalyst supported on PVF-PANI composite. *Ordu Üniversitesi Bilim ve Teknoloji Dergisi, 10(1)*, 1-10. https://dergipark.org.tr/en/pub/ordubtd/issue/55660/755194

Vigier, F., Coutanceau, C., Perrard, A., Belgsir, E. M., & Lamy, C. (2004). Development of anode catalysts for a direct ethanol fuel cell. *Journal of Applied Electrochemistry, 34*, 439-446. https://doi.org/10.1023/B:JACH.0000016629.98535.ad

Zhang, Z., Liu, Q., Pan, D., Xue, Y., Liu, X., Zhao, J., Ouyang, Y., Ding, X., Xiao, S., & Yang, Q. (2023). Formation of a PVP-protected C/UO 2/Pt catalyst in a direct ethanol fuel cell. *RSC advances*, *13*(23), 15910-15917. https://doi.org/10.1039/D3RA01017A

Singh, B. K., & Mahapatra, S. S. (2023). Performance study of palladium modified platinum anode in direct ethanol fuel cells: A green power source. *Journal of the Indian Chemical Society, 100*(2), 100876. https://doi.org/10.1039/D3RA01017A

Zhou, W., Zhou, Z., Song, S., Li, W., Sun, G., Tsiakaras, P., & Xin, Q. (2003). Pt based anode catalysts for direct ethanol fuel cells. *Applied Catalysis B: Environmental, 46(2),* 273-285. https://doi.org/10.1016/S0926-3373(03)00218-2