ESOGÜ Müh. Mim. Fak. Dergisi 2024, 32(2), 1356-1362 J ESOGU Eng. Arch. Fac. 2024, 32(2), 1356-1362

SYNTHESIS OF BENZO[B]THIOPHENE-BASED ORGANIC COMPOUNDS AND THEIR HYDRAZINE ELECTROOXIDATION PERFORMANCE AS AN ANODE CATALYST

Omruye OZOK ARİCİ[1*], Sefika KAYA[2], Aykut CAGLAR[3], Hilal KİVRAK[4], Arif KİVRAK[5]

[1] Department of Biomedical Engineering, Faculty of Engineering and Architectural Sciences, Eskişehir Osmangazi University, Eskişehir-Türkiye, ORCID No : https://orcid.org/0000-0002-4164-8650
[2] Department of Chemical Engineering, Faculty of Engineering and Architectural Sciences, Eskişehir Osmangazi University, Eskişehir-Türkiye, ORCID No : https://orcid.org/0000-0001-8277-4365
[3] Central Research Laboratory, Bartın University, Bartın-Türkiye, ORCID No : https://orcid.org/0000-0002-0681-1096
[4] Department of Chemical Engineering, Faculty of Engineering and Architectural Sciences, Eskişehir Osmangazi University, Eskişehir-Türkiye, ORCID No : https://orcid.org/0000-0001-8001-7854
[5] Department of Chemistry, Faculty of Sciences and Arts, Eskişehir Osmangazi University, Eskişehir-Türkiye, ORCID No : https://orcid.org/0000-0003-4770-2686

Keywords
Energy,
Fuel cell,
Hydrazine,
Benzothiophene,
Palladium

Abstract

In this study, 3-iodo-2-(p-tolyl)benzo[b]thiophene (4C) is synthesized by using Sonagashira coupling reactions and electrophilic cyclization reactions. Electrochemical measurements have been performed using electrochemical methods such as cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) in the environment of 1 M KOH + 0.5M N_2H_4 solution. The CV results obtained showed that 4C catalyst promoted the generation of the best current (15.40 mA/cm^2), and EIS results confirmed that electrode modifeed with the same derivative presented the lowest charge transfer resistance. Taken together, these results suggest that 4C organocatalyst could be used as an anode efficient catalyst in hydrazine (N_2H_4) fuel cells.

BENZO[B]TİYOFEN BAZLI ORGANİK BİLEŞİKLERİN SENTEZİ VE ANOT KATALİZÖRÜ OLARAK HİDRAZİN ELEKTROOKSİDASYON PERFORMANSI

Anahtar Kelimeler
Enerji,
Yakıt hücresi,
Hidrazin,
Benzotiyofen,
Paladyum

Öz

Bu çalışmada Sonagashira bağlanma reaksiyonları ve elektrofilik siklizasyon reaksiyonları kullanılarak 3-iodo-2-(p-tolil)benzo[b]tiyofen (4C) sentezlendi. Elektrokimyasal ölçümler, 1 M KOH + 0,5M N_2H_4 çözeltisi ortamında, döngüsel voltametri (CV), kronoamperometri (CA), elektrokimyasal empedans spektroskopisi (EIS) gibi elektrokimyasal yöntemler kullanılarak gerçekleştirilmiştir. Elde edilen CV sonuçları, 4C katalizörünün en iyi akımın (15.40 mA/cm^2) üretimini desteklediğini gösterdi ve EIS sonuçları, aynı türevle modifiye edilen elektrotun en düşük yük transfer direncine sahip olduğunu göstermektedir. Birlikte ele alındığında, bu sonuçlar 4C organik katalizörünün hidrazin (N_2H_4) yakıt hücrelerinde anot açısından verimli bir katalizör olarak kullanılabileceğini göstermektedir.

Araştırma Makalesi		Research Article	
Başvuru Tarihi	: 15.02.2024	Submission Date	: 15.02.2024
Kabul Tarihi	: 14.06.2024	Accepted Date	: 14.06.2024

* Sorumlu yazar: o.ozok@hotmail.com

https://doi.org/10.31796/ogummf.1437602

1. Introduction

Energy affects all aspects of our modern life (Demirbas, Sahin-Demirbas and Hilal Demirbas, 2004). Fossil fuels (such as oil, natural gas and coal) are the main energy sources all over the world in the last century Park, Lee and Kim, 2013). However, due to the growing world population and industry, the need for energy is increasing, and therefore alternative energy sources are needed to meet the energy needs. Modern electrical power generation relies on non-renewable resources. These days, new, efficient, cheap and small-scale renewable energy production options are more preferred.

Nowadays the renewable energy sources these days, fuel cells (Kivrak, Can, Duru and Sahin, 2014) organic solar cells (Yang and Forrest, 2008) and batteries (Clarke and Durrant, 2010) are at the top of the list as clean energy sources. Among these, fuel cell applications have come to the fore recently due to environmental pollution and the need for sustainable energy (Shi, Huo, Esan, An and Zhao, 2021; Wang, Li and Fooladi, 2021). Fuel cells are preferred today due to their features such as low pollution, low noise and high energy efficiency (Peng, Chen, Peng and Marefati, 2020; Wang, Chen, Mishler, Cho and Adroher, 2011). Proton exchange membrane fuel cells have been preferred in liquid fuel cell applications because they have disadvantages such as hydrogen production, storage and transportation (Khoo et al., 2021; Huang and Li, 2015). Therefore, nowadays, scientists have focused on liquid fuels because of their ease of use and high energy efficiency (Caglar and Kivrak 2019; Abdullah, Kamarudin, Hasran, Masdar and Daud, 2014).

Hydrazine (N_2H_4) is preferred in fuel cells today due to its high hydrogen content and advantages such as high negative electrooxidation potential and zero CO_2 emission with oxygen as an oxidizer (Feng et al., 2019). The reason for the need for modified electrodes in the fuel cell; the kinetic oxidation of hydrazine is difficult (Wang, Wan and Zhang, 2010; Ding et al., 2019) reported that prepared MnO/NAC catalyst exhibits high catalytic activity and showed extraordinary stability also after 3000 cycles in hydrazine electrooxidation reaction. Besides, (Wang et al., 2019), notified that P-CuxNiy/C catalysts were prepared by a high-temperature phosphating process for hydrazine electrooxidation, and among the designed catalysts, P-Cu2Ni/C exhibited the best stability and electrocatalytic activity. Apart from these catalysts, the maximum peak values of metalbased catalysts for hydrazine electrooxidation reaction compiled from the literature are given in Table 1. Today, organic molecules are preferred as catalysts in materials science because they have very important advantages such as flexibility, low molecular weight, low charge transfer resistance and high electrochemical stability. Because of the advantages of organic molecules, scientists focused on this topic (Peumans, Yakimov and Forrest, 2003). It was reported that the organic catalyst synthesized by (Er, Ulas, Ozok, Kivrak and Kivrak, 2021). showed a very high performance for hydrazine electrooxidation by showing a current of 3.22 mA/ cm^{-2}, and this organic catalyst showed the lowest charge transfer resistance. As a result, they developed that organic materials can be used instead of expensive metal catalysts as anode catalysts in N_2H_4 fuel cells.

Table 1. Maximum current density for N_2H_4 electrooxidation reported in the literature.

Catalyst	Preparation	Maximum Peak ($mA*cm^{-2}$)	Reference
MnO/N-C	dope	6.30	(Ding et al., 2019)
AuPd DANCs Co@NM NCS	co-reduction deposition dope	9.57 8.13 2.88	(Chen, Jiang, Wang, Chen and Feng, 2016) (Zhao, Sun, Chen, Huang, and Lu, 2019) (Cazetta, Zhang, Silva, Almeida and Asefa, 2018).
Organic compound	Synthesis	4.95	(Er, et al., 2021)
4C	**Synthesis**	**15.40**	**This work**

Heterocyclic molecules have wide applications in materials science (Cho, Neuenswander, Lushington and Larock, 2019). Thiophenes, benzothiophenes, indoles, furans, pyrroles, pyridines are member of known heteroaromatic compounds (Figure 1). Benzothiophene derivatives constitute an important class of very important heteroaromatic compounds. They show a lot of biological behaviors such as antitumor, analgesic, antibacterial, antiparasitic, antipyretic (Algso and Kivrak 2019; Keri et al., 2017). Benzothiophene derivatives have also been used in organic materials due to their low molecular weight and greater flexibility in organic solar cells (Morimoto et al., 2018) and transistors (Guo et al., 2018). Because of their advantages, new organic materials containing (O, S and N) have been designed and synthesized for renewable energy generation.

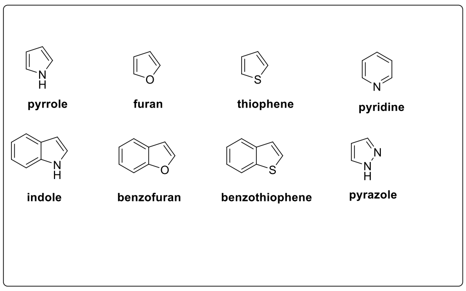


Figure 1. Some Examples of Heteroaromatic Compounds

Our study consists of two parts: organic synthesis and hydrazine electro-oxidation. In the first part, benzothiophene derivatives were designed and synthesized using sonagashira reaction and electrophilic cyclization reaction. In the second part, we aimed to design and investigate synthesized organic catalysts as a new organic anode catalyst for the oxidation of hydrazine in fuel cells. (CV), spectroscopy (EIS) and (CA) methods were used for electrochemical measurements.

2. Material and Methods

2.1. Synthesis of organic catalysts

General Procedure for the synthesis of methyl (2-(aryl/alkyl-ethynyl) phenyl) sulfane 3: To a solution of 2-iodo thioanisole (1 eq) in Et3N (15 mL) and THF (10 mL) was added alkyne (1.2 eq), Pd(PPh3)2Cl2 (2%), and CuI (1%) argon atmosphere. The mixture was stirred at room temperature (room) overnight. After the starting compound was completely consumed, the mixture was extracted and the organic phase was dried with anhydrous MgSO4. After filtration, the solvent was evaporated under high pressure and the residue was purified by column chromatography using the Hexane solvent system to give 3 (Figure 2).

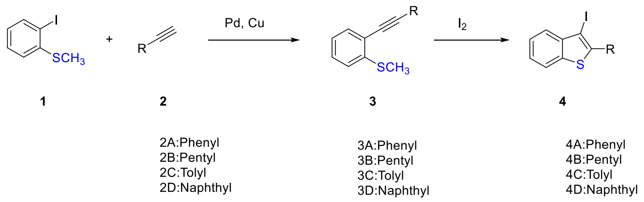


Figure 2. Synthesis of 3-iodo-benzothiophene Derivatives 4A-D

Methyl(2-(phenylethynyl)phenyl)sulfane (3A): 2-Iodothioanisole (4 mmole), phenylacetylene (4.8 mmole), $PdCl_2(PPh_3)_2$ (0.33 mmole), CuI (0.017 mmole), THF (10 mL) and Et_3N (15 mL) were employed to afford 880 g of the desired compound as yellow color, yield 92%; Solvent: Hexane. The spectral data have been previously reported for this compound. (Er et al., 2021).

(2-(hept-1-yn-1-yl)phenyl)(methyl)sulfane (3B): 2-Iodothioanisole (4 mmole), 1-heptyne (4.8 mmole,), $PdCl_2(PPh_3)_2$ (0.33 mmole), CuI (0.017 mmole), THF (10 mL) and Et_3N (15 mL) were employed to afford 825 mg of the desired compound as a brown color, yield 94%; Solvent: Hexane/EtOAc (100/1); The spectral data have been previously reported for this compound. (Er et al., 2021).

Methyl(2-(p-tolylethynyl)phenyl)sulfane (3C): 2-Iodothioanisole (4 mmole), 4-ethynyltoluene (9.6 mmole), $PdCl_2(PPh_3)_2$ (0.33 mmole), CuI (0.017 mmole), THF (10 mL) and Et_3N (15 mL) were employed to afford 790 mg of the desired compound as a yellow color, yield 88%; Solvent: Hexane/EtOAc (100/1). The spectral data have been previously reported for this compound. (Er et al., 2021).

Methyl(2-(naphthalen-1-ylethynyl)phenyl)sulfane (3D): 2-Iodothioanisole (4 mmole), 1-ethynylnaphthalene (4.8 mmole), $PdCl_2(PPh_3)_2$ (0.33 mmole), CuI (0.017 mmole), THF (10 mL), and Et_3N (15 mL) were employed to afford 790 mg of the desired compound as a white, yield 72%; Solvent: Hexane/EtOAc (100/1). The spectral data have been previously reported for this compound (Er et al., 2021).

General Procedure for the synthesis of 3-iodo-2-aryl/alkyl-benzo[b]thiophene (4): To a solution of methyl(2-(aryl/alkyl-ethynyl)phenyl)sulfan 3 in 20 mL of DCM was added molecular iodine (2 eq.) under argon atmosphere. The mixture was stirred at rt for 3 hours. After the starting material was completely completed, the mixture was extracted into DCM and the organic phase was dried over anhydrous $MgSO_4$. After filtration, the residue was purified by column chromatography using Hexane/EtOAc to give (4).

3-Iodo-2-phenylbenzo[b]thiophene 4A: 3A (3.4 mmole), DCM (20 mL), I_2 (6.8 mmole) were employed to afford 965 mg of the desired compound, yield 86%; Solvent: Hexane; The spectral data have been previously reported for this compound (Ozok, Kavak, Er, Kivrak and Kivrak, 2020).

3-Iodo-2-pentylbenzo[b]thiophene 4B: 3B (4 mmole), DCM (20 mL), I_2 (8 mmole) were employed to afford 1.7 g of the desired compound, yield 95%; Solvent: Hexane. The spectral data have been previously reported for this compound (Ozok et al., 2020).

3-iodo-2-(p-tolyl)benzo[b]thiophene 4C: 3C (3.2 mmole), DCM (20 mL), I_2 (6.4 mmole) were employed to afford 902 mg of the desired compound, yield 79%; Solvent: Hexane. The spectral data have been previously reported for this compound (Ozok et al., 2020).

3-Iodo-2-(naphthalen-1-yl)benzo[b]thiophene (4D): 3D (2.7 mmole), DCM (20 mL), I2 (5.4 mmole) were employed to afford 746 mg of the desired compound, yield 75%; Solvent: Hexane. The spectral data have been previously reported for this compound (Ozok et al., 2020).

2.2. Electrochemical measurements

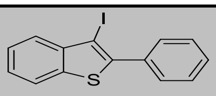
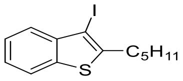
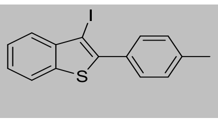
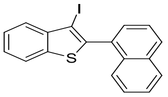
Electrochemical measurements were implemented employing the CHI 660E potentiostat device to determine the glucose electrooxidation activities of the catalysts. CV, CA, and EIS measurements were performed in a three-electrode system consisting of glassy carbon electrode (working electrode), Pt wire (counter electrode), and Ag/AgCl (reference electrode) in 1 M KOH + 1 M N_2H_4 solution. The electrooxidation activities of the catalysts were determined via CV at 50 mV/s at the potential range of -0.6-0.8 V. CA measurements for the stability of 4C catalyst was performed at 0.0, 0.2, 0.4 V, 0.6 and 0.8V potentials at 1000 s. The electrochemical resistance of this catalyst was investigated by EIS at 316 kHz-0.046 Hz frequency and 5 mV amplitude.

3. Results and Discussion

3.1. Synthesis

The Sonogashira coupling reaction is one of the most important reactions in organic chemistry that allows the formation of new c-c bonds. In the first part, 2-iodothiyanisol **(1)** was allowed to react with primary alkynes **(2)** in the presence of Pd catalyst at rt under inert atmosphere and intermediate **(3)** was obtained with high yields. In this step, our 3D organic catalyst was synthesized with the highest efficiency of 94%. In the next step, electrophilic cyclization reaction was used in iodine medium and derivatives **(4)** were synthesized. The yields of the isolated molecules vary between 75% and 95% (Table 2).

Table 2. Yields of 3-iodo-benzothiophene Derivatives 4A-D.

ENTRY	PRODUCT	YIELD
1		4A 86%
2		4B 95%
3		4C 78%
4		4D 75%

3.2. Electrochemical results

The (heo) activity of 4A-D organic catalysts was investigated by CV analysis. CV measurements were taken in 1 M KOH and 1 M KOH + 0.5 M N_2H_4 solutions in the potential range (0.0 V - 0.8 V). Since no oxidation peak was observed in N_2H_4 measurements, organocatalysts were evaluated based on total current. (Figure 3). In heo, 15.406 mA/cm^2 was determined as the **4C** catalyst, which showed the highest current performance among organocatalysts (Table 3).

In Figure 3b, it was seen that the current intensity of hydrazine electrooxidation was due to the different chemical structures of the benzothiophene derivatives. The highest heo current is the **4C** derivative to which the tolyl primary alkyne is attached. The CV stability of the **4C** catalyst was taken at potentials of 0.0 V to 0.8 V in 1 M KOH + 0.5 M N_2H_4 solution. As mentioned above, the highest heo current obtained from CV results was obtained from (4C). In addition, the highest stability was obtained at 4C. It has been observed that the presence of tolyl groups in the chemical structure increases electrooxidation activity and stability.

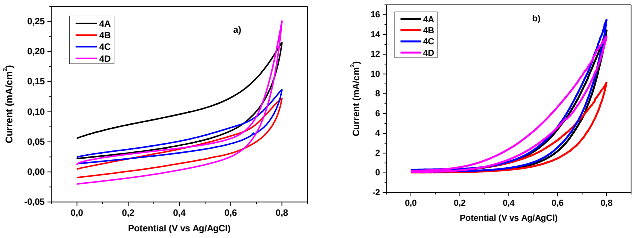


Figure 3. CV results of organocatalysts 4(A-D) in a) 1 M KOH and b) 1 M KOH + 0.5 M N_2H_4

Table 3. N_2H_4 electrochemical results of organocatalysts

Catalyst	Total Current of KOH, mA/cm^2	Total Current of N_2H_4, mA/cm^2	Normal Current, mA/cm^2
4A	0.215	14.375	14.160
4B	0.121	9.136	9.015
4C	0.137	**15.406**	**15.269**
4D	0.251	13.755	13.504

Chronoamperometry curves can be used to determine the stability and catalytic activity of electrocatalysts (Kivrak et al., 2014). For this purpose, CA measurements were performed in 1 M KOH + 1 M N_2H_4 solution at different potential values (0.0, 0.2, 0.4, 0.6, and 0.8 V) in 1000 seconds (Figure 4a). Since the 4C organocatalyst exhibited greater long-term stability and the highest current, it was measured to have higher activity among other catalysts according to electrical distribution values (Figure 4b). These results showed the best stable structure of the 4C organocatalyst at 0.8V for a long time.

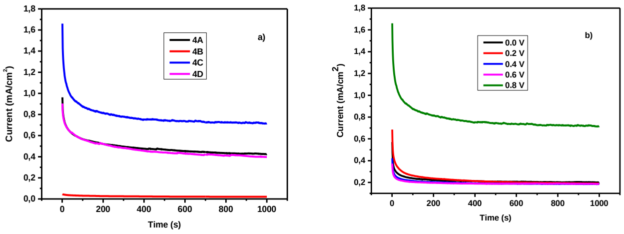


Figure 4 a) CA Results of Organocatalysts at 0.8 V, b) CA Analysis of Organocatalyst 4C.

EIS measurements are often used to calculate electrocatalytic resistance, with the diameter of the circle decreasing as resistance increases (Sahin, Duzenli and Kivrak, 2016). Figure 5a shows plotted Nyquist Plots of 4C catalyst at 0.0-0.2-0.4-0.6-0.8V potentials. Figure 5b also shows the comparison of EIS results for organocatalysts at 0.8 V. Figure 5c shows that the transfer resistor load is 4C > 4D > 4B > 4A. The electrocatalytic activities of the catalysts are determined by relating the diameter of these semicircles to the charge transfer resistance (Ulas, Caglar, Sahin and Kivrak, 2018). The charge transfer resistance (R_{ct}) values of GCE electrode modified with 4C in 0.8 V (2747 Ω) > 0.6 V (5102 Ω) > -0.0 V (5203 Ω) > -0.2 V (5408 Ω), > 0.4 V (5825 Ω), different potentials was found from the equivalent circuit model. Since 0.8 V potential has the lowest semicircular shape and R_{ct}, it has the highest carrier transfer performance compared to other potentials.

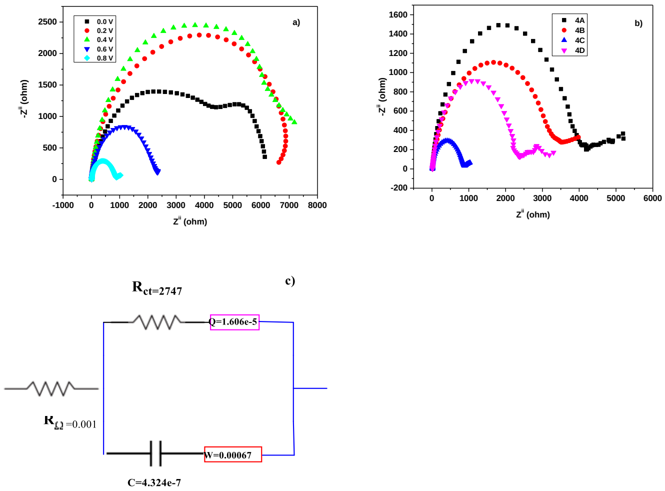


Figure 5. Nyquist Graph Obtained in 1M KOH + 0.5 M N_2H_4 Solution a) 4C Catalyst Different Potentials and b) Compared to All Other Organocatalysts at 0.8 V in 1 M KOH + 0.5 M N_2H_4,c) The Charge Transfer Resistance (Rct) Values of 4C Electrode.

As a result, the 4C electrocatalyst exhibited the highest electrocatalytic activity when compared to organacatalysts. When the results were examined, it was seen that CV and CA were compatible with the results.

5. Conclusions

This study consists of two parts. The first part is the synthesis of organic-based catalysts. In the first step of the synthesis, new C-C bonds were formed using the Sonogashira Coupling reaction under Pd catalysis. In the next step, 3-iodobenzothiophene derivatives were synthesized and characterized using electrophilic cyclization reactions. The second part is testing the hydrazine electrooxidation of catalysts. Electrochemical measurements were made by (CV), (CA) and (EIS) in 1 M KOH + 0.5 M N_2H_4 solution. 4C (15.40 mA/cm^2) showed activity as the highest performance organic base in hydrazine electrooxidation. In addition, 4C is the organocatalyst with long-term stability and highest current. It has been found that a metal-free organic molecule shows a high current compared to studies in the literature. In conclusion, the 4C benzothiophene derivative may be promising as an alternative to expensive metals such as Pd and Pt.

Acknowledgement

The authors thank to Eskişehir Osmangazi University BAP (Project No: FOA-2021-2203) for chemicals and solvents. The author (A. Kivrak) would like to acknowledge networking contribution by the COST Action CA17104 “New diagnostic and therapeutic tools against multidrug resistant tumours”.

Author Contributions

In the study, Omrüye OZOK ARİCİ contributed to the literature review, writing the article, and interpreting the data. Şefika KAYA and Aykut ÇAGLAR contributed to the laboratory studies. Hilal KİVRAK and Arif KİVRAK contributed to the evaluation and analysis of the results.

Conflict of Interest

There is no conflict of interest with any person/institution in the prepared article.

References

Abdullah, S., Kamarudin, S.K., Hasran, U.A., Masdar, M.S. & Daud, W.R.W. (2014). Modeling and simulation of a direct ethanol fuel cell: An overview. *Journal of Power Sources*, 262, 401-406. doi: https://doi.org/10.1016/j.jpowsour.2014.03.105

Algso, M.A. & Kivrak, A. (2019). New strategy for the synthesis of 3-ethynyl-2-(thiophen-2-yl) benzo [b] thiophene derivatives. *Chemical Papers*, 73(4), 977-

985. doi: https://doi.org/10.1007/s11696-018-0640-2

Caglar, A. & Kivrak, H. (2019). Highly active carbon nanotube supported PdAu alloy catalysts for ethanol electrooxidation in alkaline environment. *International Journal of Hydrogen Energy*, 44(23), 11734-11743. doi: https://doi.org/10.1016/j.ijhydene.2019.03.118

Cazetta, A.L., Zhang, T., Silva, T.L., Almeida, V.C. & Asefa, T. (2018). Bone char-derived metal-free N-and S-co-doped nanoporous carbon and its efficient electrocatalytic activity for hydrazine oxidation. *Applied Catalysis B: Environmental*, 225, 30-39. doi: https://doi.org/10.1016/j.apcatb.2017.11.050

Chen, L. X., Jiang, L. Y., Wang, A. J., Chen, Q. Y. & Feng, J. J. (2016). Simple synthesis of bimetallic AuPd dendritic alloyed nanocrystals with enhanced electrocatalytic performance for hydrazine oxidation reaction. *Electrochimica Acta*, 190, 872-878. doi: https://doi.org/10.1016/j.electacta.2015.12.151

Cho, C.H., Neuenswander, B., Lushington, G.H. & Larock, R.C. (2019). Solution-phase parallel synthesis of a multi-substituted benzo [b] thiophene library. *Journal of combinatorial chemistry*, 11(5), 900-906. doi: https://doi.org/10.1021/cc9000604

Clarke, T.M. & Durrant, J.R. (2010). Charge photogeneration in organic solar cells. *Chemical reviews*, 110(11), 6736-6767. doi: https://doi.org/10.1021/cr900271s

Demirbas, A., Sahin-Demirbas, A. & Hilal Demirbas, A. (2004). Global energy sources, energy usage, and future developments. *Energy Sources*, 26(3), 191-204. doi: https://doi.org/10.1080/00908310490256518

Ding, J., Kannan, P., Wang, P., Ji, S., Wang, H., Liu, Q., Gai, H., Liu, F. & Wang, R. (2019). Synthesis of nitrogen-doped MnO/carbon network as an advanced catalyst for direct hydrazine fuel cells. Journal of Power Sources, 413, 209-215. doi: https://doi.org/10.1016/j.jpowsour.2018.12.050

Er, O.F., Ulas, B., Ozok, O., Kivrak, A. & Kivrak, H., (2021). Design of 2-(4-(2-pentyllbenzo [b] thiophen-3-yl) benzylidene) malononitrile based remarkable organic catalyst towards hydrazine electrooxidation. *Journal of Electroanalytical Chemistry*, 888, 115218. doi: https://doi.org/10.1016/j.jelechem.2021.115218

Feng, Z., Li, D., Wang, L., Sun, Q., Lu, P., Xing, P. & An, M. (2019). In situ grown nanosheet NiZn alloy on Ni foam for high performance hydrazine electrooxidation. *Electrochimica Acta*, 304, 275-281. doi: https://doi.org/10.1016/j.electacta.2019.03.017

Guo, S., He, Y., Murtaza, I., Tan, J., Pan, J., Guo, Y., Zhu, Y., He, Y. & Meng, H. (2018). Alkoxy substituted [1] benzothieno [3, 2-b][1] benzothiophene derivative with improved performance in organic thin film transistors. *Organic Electronics*, 56, 68-75. doi: https://doi.org/10.1016/j.orgel.2018.02.003

Huang, W.T. & Li, Y. (2015). Electrical characteristic fluctuation of 16-nm-gate trapezoidal bulk FinFET devices with fixed top-fin width induced by random discrete dopants. *Nanoscale research letters*, 10(1), .1-8. doi: https://doi.org/10.1007/s12633-023-02835-3

Keri RS, Chand K, Budagumpi S, Somappa SB, Patil SA, & Nagaraja BM. (2017). An overview of benzo[b]thiophene-based medicinal chemistry. *Eur J Med Chem*. 138:1002–1033. doi: https://doi.org/10.1016/j.ejmech.2017.07.038

Khoo, K.S., Chia, W.Y., Wang, K., Chang, C.K., Leong, H.Y., Maaris, M.N.B. & Show, P.L. (2021). Development of proton-exchange membrane fuel cell with ionic liquid technology. *Science of The Total Environment*, 793, 148705. doi: https://doi.org/10.1016/j.scitotenv.2021.148705

Kivrak, H., Can, M., Duru, H. & Sahin, O. (2014). Methanol electrooxidation study on mesoporous silica supported Pt–Co direct methanol fuel cell anode. *International Journal of Chemical Reactor Engineering*, 12(1), 369-375. doi: https://doi.org/10.1515/ijcre-2014-0051

Morimoto, M., Takagi, Y., Hioki, K., Nagasaka, T., Sotome, H., Ito, S., Miyasaka, H. & Irie, M. (2018). A turn-on mode fluorescent diarylethene: solvatochromism of fluorescence. *Dyes and Pigments*, 153, 144-149. doi: https://doi.org/10.1016/j.dyepig.2018.02.016

Park, M., Lee, T. & Kim, B.S. (2013). Covalent functionalization based heteroatom doped graphene nanosheet as a metal-free electrocatalyst for oxygen reduction reaction. *Nanoscale*, 5(24), 12255-12260. doi: https://doi.org/10.1039/C3NR03581F

Peng, M.Y.P., Chen, C., Peng, X. & Marefati, M. (2020). Energy and exergy analysis of a new combined concentrating solar collector, solid oxide fuel cell, and steam turbine CCHP system. *Sustainable Energy Technologies and Assessments*, 39, 100713. doi: https://doi.org/10.1016/j.seta.2020.100713

Peumans, P., Yakimov, A. & Forrest, S.R. (2003). Small molecular weight organic thin-film photodetectors and solar cells. *Journal of Applied Physics,* 93(7), 3693-3723. doi: https://doi.org/10.1063/1.1534621

Sahin, O., Duzenli, D. & Kivrak, H. (2016). An ethanol electrooxidation study on carbon-supported Pt-Ru nanoparticles for direct ethanol fuel cells. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 38(5), 628-634. doi: https://doi.org/10.1080/15567036.2013.809391

Shi, X., Huo, X., Esan, O.C., An, L. & Zhao, T.S. (2021). Performance characteristics of a liquid e-fuel cell. *Applied Energy*, 297, 117145. doi: https://doi.org/10.1016/j.apenergy.2021.117145

Ozok, O., Kavak, E., Er, O.F., Kivrak, H. & Kivrak, A. (2020). Novel benzothiophene based catalyst with enhanced activity for glucose electrooxidation. *International Journal of Hydrogen Energy*, 45(53), 28706-28715. doi: https://doi.org/10.1016/j.ijhydene.2020.07.195

Ulas, B., Caglar, A., Sahin, O. & Kivrak, H. (2018). Composition dependent activity of PdAgNi alloy catalysts for formic acid electrooxidation. *Journal of colloid and interface science*, 532, 47-57. doi: https://doi.org/10.1016/j.jcis.2018.07.120

Wang, W., Wang, Y., Liu, S., Yahia, M., Dong, Y. & Lei, Z. (2019). Carbon-supported phosphatized CuNi nanoparticle catalysts for hydrazine electrooxidation. *International Journal of Hydrogen Energy*, 44(21), 10637-10645. doi: https://doi.org/10.1016/j.ijhydene.2019.03.005

Wang, S., Li, W. & Fooladi, H. (2021). Performance evaluation of a polygeneration system based on fuel cell technology and solar photovoltaic and use of waste heat. *Sustainable Cities and Society*, 72, 103055. doi: https://doi.org/10.1016/j.scs.2021.103055

Wang, Y., Chen, K.S., Mishler, J., Cho, S.C. & Adroher, X.C. (2011). A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research. *Applied energy*, 88(4), 981-1007. doi: https://doi.org/10.1016/j.apenerg.2010.09.030

Wang, Y., Wan, Y. & Zhang, D. (2010). Reduced graphene sheets modified glassy carbon electrode for electrocatalytic oxidation of hydrazine in alkaline media. *Electrochemistry Communications*, 12(2), 187-190. doi: https://doi.org/10.1016/j.elecom.2009.11.019

Yang, F. & Forrest, S.R. (2008). Photocurrent generation in nanostructured organic solar cells. *ACS nano*, 2(5), 1022-1032. doi: https://doi.org/10.1021/nn700447t

Zhao, A., Sun, H., Chen, L., Huang, Y. & Lu, X. (2019). Development of highly efficient and scalable free-standing electrodes for the fabrication of hydrazine-O2 fuel cell. *Materials Research Express*, 6(8), 085533. doi: https://doi.org/10.1088/2053-1591/ab242f