

Catalytic electro-oxidation of hydrazine by thymol based-modified glassy carbon electrode

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ABSTRACT

In the present, thymol based new organic compounds (**4A**, **4B** and **4C**) are designed and synthesized via Steglich Esterification Reactions and Pd-catalyst Sonogashira Coupling Reactions. After isolation and characterization, thymol based hybrid molecules are used for hydrazine (N₂H₄) electrooxidation reactions as anode catalysts. A variety of metal based anode catalyst have been reported in literature, but this study may be the first study for thymole based hybrid molecules as an anode catalyst in fuel cells. The performance of hybrid molecules was investigated via cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in hydrazine solution. Hybrid 2-isopropyl-5-methylphenyl-4-oxo-4-(5-(p-tolylethynyl)thiophen-2-yl)butanoate (**4C**) gives the highest performance as 3.66 mAcm⁻² (17.24 mAcmg⁻¹). Our results displayed that natural products like thymol derivatives may be new generation anode catalyst for fuel cells, and they may be alternative for expensive Pd and Pt based metal anode catalyst.

1. Introduction

Energy is an essential component for human life. Increasing world-wide energy demand associated with fossil resources creates the energy crisis in the next two or three decades [1]. Fossil energy has been become expensive and scarce, while fossil fuels are not environmentally friendly, and they also cause the climate change due to greenhouse gases. At the present time, existing fossil energy sources are not abandoned, but renewable energy sources are reduced or eliminated their environmental impact [2–3]. New technologies may help to discover new clean energy sources to decrease the greenhouse gas effects in the next few decades [4–5]. Nowadays, scientists are trying to new ways to produce the clean energy by using solar cells [6–7], wind power, hydroelectric power and nuclear plants [8]. In addition, alternative methods including fuel cells [9,10], batteries [11], biomass [12] and hydrogen sources have been used for the producing energy [13].

Fuel cells convert the chemical energy to cleanly and efficiently electricity. There are the variety of potential applications of fuel cells; they can be used not only plants for industrial applications, but also small electronic devices like laptops. Fuel cells have many advantages

such as; the efficiency (higher than 60 %), ii) lower carbon dioxide emissions, iii) environmentally friendly technologies due to the only water was formed as side product. Moreover, hydrazine fuel cells do not cause the air pollutants [14,15]. Fuel cells produce electricity and heat without run down and recharging. Fuel cell consists of two electrodes; an anode (or negative electrode) and a cathode (or positive electrode). When hydrogen is used as fuel in cells, hydrogen molecules form protons and electrons in anode catalyst surface. The electrons create a flow of electricity. At the same time, the protons move to the cathode to form the water and heat.

Although fuel cells are considered to be next generation clean energy sources, but there are some key challenge (cost, performance, and durability) for fuel cell development [16–19]. Metals like platinum, gold, palladium are mainly used as anode catalyst in direct hydrogen fuel cells, so new catalyst systems are designed to decrease the cost. For example, polymer membrane fuel cell was used to reduce the content of heavy metals, or metal-free polymers were investigated as anode catalyst for fuel cell applications. Secondly, improving fuel cell efficiency and performance is the very important to design of new catalysts for future applications. In addition, lifetime of fuel cell is also main

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Table 1
The anode catalysts performance of hydrazine electro-oxidation in fuel cells.

Catalyst	Preparation	Maximum Peak (mA*cm ⁻²)	Reference
PPY/NOCB/900	polymerization	1.84	[34]
Wash-CN _{Cu}	Dope	1.94	[35]
Benzothiophene	organic synthesis	4.95	[31]
NiFe ₂ O ₄ -rGO	hydrothermal method	18.9	[36]
(PpPD/ZnO)	Dope	0.172	[37]

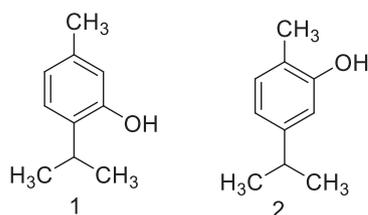
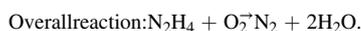
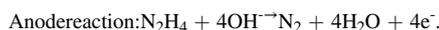


Fig. 1. Structure of Thymol (1) and Carvacrol (2).

problems under realistic operating conditions. Therefore, many scientist focused on investigate new materials for the chemical and mechanical stability.

Hydrazine [20], glucose [21], formic acid [22], ethanol [23], and methanol [24,25] are the well known fuel sources in cells. Hydrazine, N₂H₄, has very critical roles in industrial applications, explosive materials, propellants and other applications [26]. Hydrazine are also important for the producing energy in direct hydrazine fuel cells. Hydrazine is not expensive, has high energy density. In addition, it has higher performance, and it can be easily storage [27]. However, kinetically oxidation of hydrazine is not easy, so it needs special or modified electrodes in fuel cell [28]. The electrooxidation reactions of hydrazine in alkaline medium can be written as the following equations:



To increasing efficiencies of cells, metals including platinum, silver, gold and cobalt were modified and tested as electrocatalyst for hydrazine oxidation [29,30]. Recently, organic catalyst consisting of benzothiophenes were used for hydrazine electrooxidation, and the activity was reported as 3.22 mAcm⁻² with lowest charge transfer resistance [31]. They improved that organic compounds can be used as anode catalyst in fuel cells instead of expensive metal catalyts (Pt, Pd and Au) [32,33]. Recently, PPY/NOCB/900 [34], Wash-CN_{Cu} [35], NiFe₂O₄-rGO [36] and (PpPD/ZnO) [37] catalyst systems were prepared for fuel cell as anode catalysts. Interestingly, the best performance was obtained from NiFe₂O₄ catalysts system with 18.9 mAcm⁻² (Table 1).

Lastly, different kinds of organic compounds have been tested for the formation of clean energy including solar cells and electrochromic devices. Organic molecules are preferred for material chemistry due to

their important properties such as flexibility, lower molecular weight, charge transfer capacities, and high electrochemical stability [38–40].

Thymol [41,42] (5-methyl-2-isopropyl phenol) is the member of phenols, and isolated from thyme (*Thymus vulgaris*), oregano (*Origanum vulgare*), ajowan (*Trachyspermum ammi*), and other plants (Fig. 1) [41,43]. Thymol and its derivatives have been played very important in medicines, food, and cosmetic applications [44]. Carvacrol is the other isomer of thymols. In literature, a variety of thymol and carvacrol derivatives were synthesized for the investigation of biological properties. They have been used as anticancer, antifungal, antimicrobial, antiparasitic and antioxidant agents. Moreover, they have been used as herbicides [45]. Recently, Rajkumar *et al.* was investigated electronic properties, ionization potential, thermodynamic properties and electron affinities, inter-molecular interactions of thymole structure [46]. They found that the energies of molecular orbital, obtained excitation from HOMO to LUMO, displayed π - π^* transition.

In the present study, novel thymol based hybrid molecules are designed and synthesized by using esterification reactions and coupling reactions. Then, thymol hybrid molecules were tested as anode catalysts for hydrazine electrooxidation. In literature, variety of metal based anode catalyst have been used for the producing clean energy in fuel cells, but there are not any study including thymole and thymole derivatives as an anode catalyst. Therefore, this study could be created new generation anode catalyst system for future applications in fuel cells. Thymol and derivatives may be alternative anode catalyst for the producing electricity in direct hydrazine fuel cells.

2. Results and discussion

2.1. Synthesis

Initially, the reaction between 2 and iodothiophene and succinic anhydride gave the Friedel-Crafts reaction at room temperature to form the 4-(5-iodothiophen-2-yl)-4-oxobutanoic acid which was used directly for esterification reactions due to stability problems (SI). Then, Steglich reaction was applied for the formation of 1-(5-iodothiophen-2-yl)-4-(2-isopropyl-5-methylphenyl)butane-1,4-dione (3). When thymol was allowed to react with the intermediate in the presence of EDCl/DMAP catalyst medium, desired product 3 was obtained. After characterization of compound 3, Pd(II)-catalyzed Sonagashira coupling reaction was used for the formation of final thymol based hybrid molecules (4A-C). The 4A, 4B and 4C hybrid molecules are obtained as 79 %, 89 % and 90 % yields, respectively (Fig. 2). The proton and carbon NMR spectra of thymol derivatives have characteristics thymol's peaks, so they were easily identified. For example, thymol's protons can be identified easily in aromatic region. There are two different methyl peaks in proton NMR spectra, and there are two carbonyl's peaks around 190 ppm and 171 ppm at ¹³C NMR spectra.

2.2. Electrochemical evaluation

The electrochemical behaviors of catalysts were achieved by cyclic voltammetry analysis (potential: 0.0 and 0.8 V; scan rate: 50 mVs⁻¹). The CV analyses of catalysts in KOH (1 M) and KOH (1 M) + hydrazine (0.5 M) were shown in Fig. 3(a-c). Since the catalysts were organic-based and did not contain precious metals such as Pd, Pt, Au, it was

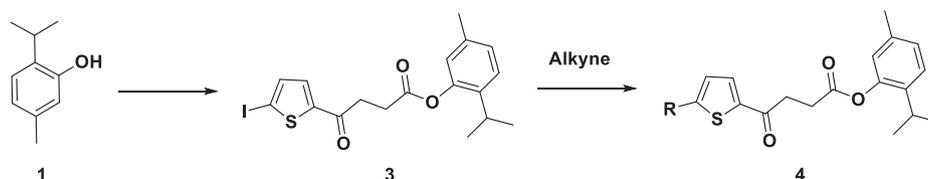


Fig. 2. Synthesis thymol based hybrid molecules (4).

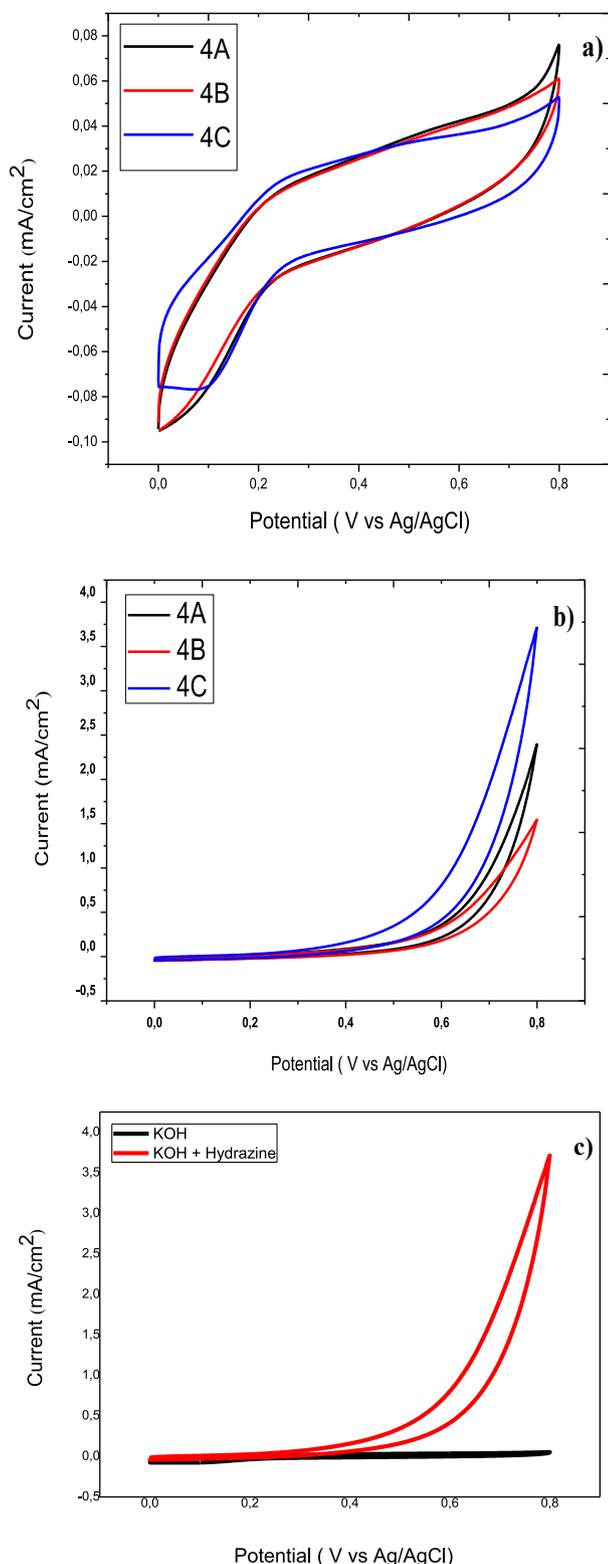


Fig. 3. Cyclic voltammety results (a) 1 M KOH; (b) 1 M KOH + 0.5 M hydrazine; (c) comparison of 1 M KOH and 1 M KOH + 0.5 M hydrazine. (Scan rate: 50 mV s⁻¹).

seen that oxidation peaks were not formed in hydrazine electrooxidation. Therefore, thymol based hybrid catalysts were calculated on the total current (Table 2). In the present study, the catalytic activities of the hybrid molecules were found by using the total current values in KOH and hydrazine mixture. It was seen in Fig. 3b and Table 2, the

Table 2

The electrochemical results from the hydrazine electrooxidation.

Hybrid	Total current (mA.cm ⁻²)		Mass Activity (mA.mg ⁻¹ catalyst)	Onset Potential (V)	
	KOH	Hydrazine	Normal		
Hybrid A	0.077	2.41	2.33	10.96	0.30
Hybrid B	0.061	1.54	1.48	6.96	0.31
Hybrid C	0.053	3.71	3.66	17.24	0.27

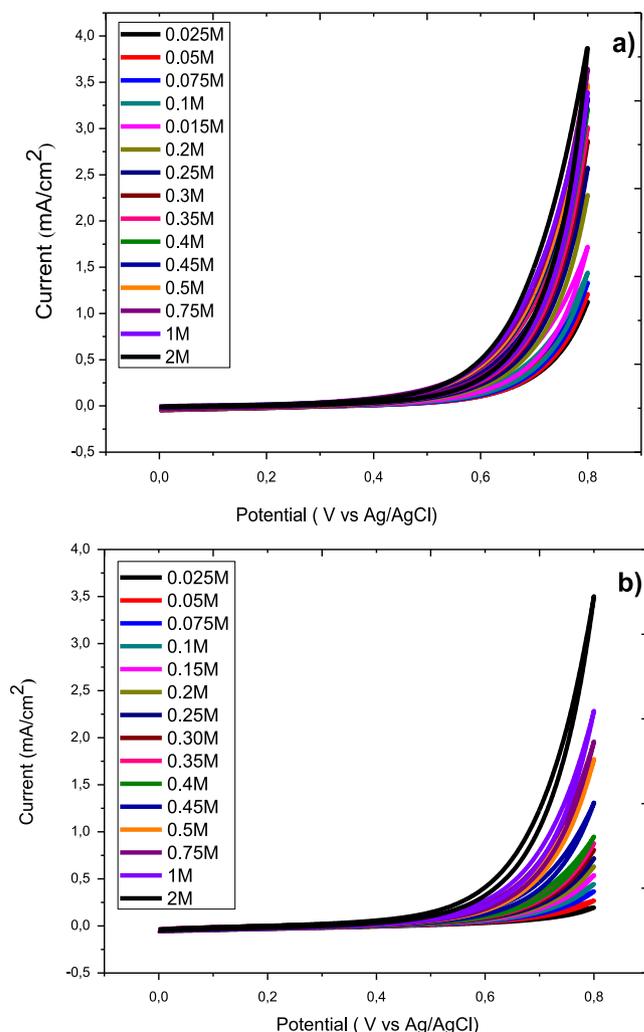


Fig. 4. CV analysis (a) different KOH concentrations with 0.5 M Hydrazine; (b) different hydrazine concentrations with 1 M KOH. Scan rate: 50 mV/s.

hybrid 4C exhibited the better activity compared to the 4A and 4B. The specific activity at the total current (Hydrazine) was calculated as 3.66 mA.cm⁻² (17.24 mA.mg⁻¹ catalyst). Fig. 3c showed a comparison of hybrid 4C not only 1 M KOH, but also KOH (1 M) + hydrazine (1/2 M) solutions. The 3.66 mA.cm⁻² specific activity is the catalytic activity obtained from hydrazine sources. Our electrochemical results improved that thymol natural product and derivatives may be alternative anode catalyst for the hydrazine fuel cells.

Hybrids 4(A-C) catalysts were tested for the investigation of hydrazine electrooxidation performances via cyclic voltammety analysis. Cyclic voltammety measurements are given in Fig. 3 in the presence of

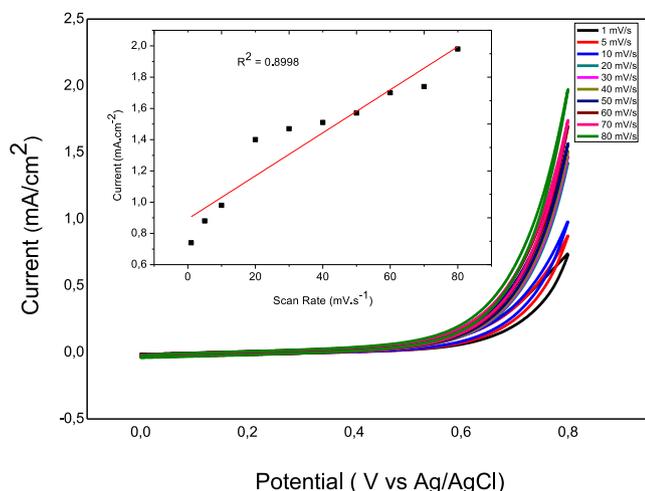


Fig. 5. CV analysis of hybrid 4C catalyst at different scan rates (1–80 $\text{mV}\cdot\text{s}^{-1}$). Inset of graph: plots of current against scan rate.

KOH (1 M) solution and KOH (1 M) + M N_2H_4 (0.5) solution.

The effect of KOH (a) and hydrazine (b) concentration change of hybrid 4C organic-based catalyst on hydrazine electrooxidation was researched and the results were given in Fig. 4 (a, b). The catalytic activity of hybrid 4C for hydrazine electrooxidation was examined by keeping the hydrazine concentration constant at 0.5 M and modifying the KOH concentrations between 0.025 and 2 M (Fig. 4a). As seen in Fig. 4a, the catalytic activity increased as the KOH concentration increased. The effect of hydrazine concentration for hydrazine electrooxidation was found by using the 1 M KOH and different concentrations of hydrazine mixtures (0.025 M to 2 M) (Fig. 4b). Interestingly, the catalytic activity increased when hydrazine concentration increased in KOH solution. The analysis of the hybrid 4C organic-based catalyst taken at different scan rates is shown in Fig. 5 (a, b). The scan rate effect was also investigated. The range changed between 1 and 80 $\text{mV}\cdot\text{s}^{-1}$ on the hybrid 4C organic-based catalyst in 1 M KOH + 0.5 M hydrazine. As shown in Fig. 5a, when scan rates (1–80 $\text{mV}\cdot\text{s}^{-1}$) increased, the catalytic activity increased. If current ($\text{mA}\cdot\text{cm}^{-2}$) values were plotted against the square root of the scan rate ($\text{mV}\cdot\text{s}^{-1}$) (inset of the graph), the current value increase and varied linearly with scan rate. It means that diffusion controlled kinetics for hydrazine electrooxidation was observed.

Chronoamperometry (CA) measurements helped to appraise the stability, and displayed poison resistance of thymol hybrid molecules. Fig. 6(a) demonstrates the CA curves of hybrid 4C organic catalyst at different potentials. Chronoamperometry analysis gave the best resistance and good stability at 0.0 V potential. Hybrid 4C organic catalyst has better activity and high stability ($0.28 \text{ mA}\cdot\text{cm}^{-2}$ specific activity) after 1000 s (Fig. 6b). CV results displayed that hybrid 4C organic-based catalyst gave the best activity. Moreover, hybrid 4C found as most stable organic catalyst when compared to other thymol based catalysts.

Fig. 7(a, b) shows the Nyquist plots obtained from the EIS was used for the investigation of the electrocatalytic resistance of the thymol hybrid catalysts (4A–C). EIS measurements usually give the semicircles to calculate the electrocatalytic resistance. When resistance increases, the diameter of the circle decrease [47,48]. Fig. 7a indicates the Nyquist plots of the hybrid 4C organic-based catalyst taken at different potentials (0.2, 0.4, 0.6, and 0.8 V). As seen in Fig. 7a, if the Nyquist plot taken at the 0.8 V, the high electrochemical resistance was obtained. Fig. 7b demonstrates the Nyquist plots of 4A, 4B, and 4C thymol organic-based catalysts at 0.8 V potential. Hybrid 4C organic-based catalyst gives smaller R_{ct} value than 4A and 4B. EIS results also improved that the thymol hybrid molecule 4C has the best catalytic activity, high stability, and lower resistance in direct hydrazine fuel cell applications.

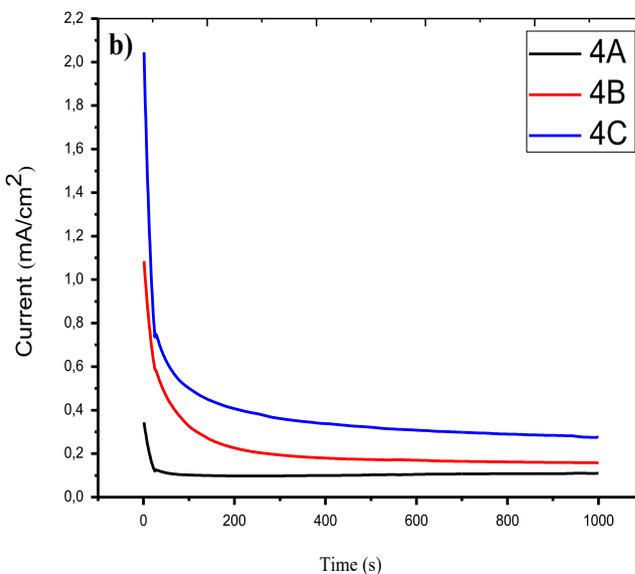
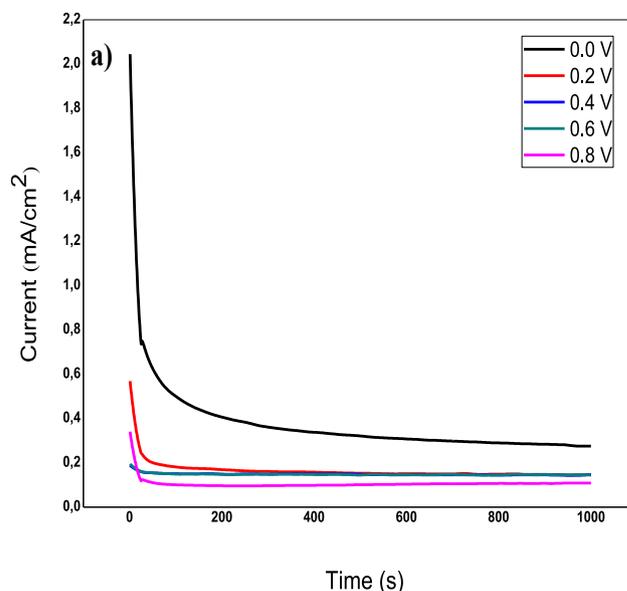


Fig. 6. CA analysis of (a) hybrid 4C, (b) hybrid 4A, hybrid 4B and hybrid 4C.

3. Conclusions

Herein, novel thymol based hybrid compounds (4A–C) are synthesized via Steglich Esterification and Sonogashira coupling reactions. Initially, 4-(5-iodothiophen-2-yl)-4-oxobutanoic acid were prepared by starting from 2 to iodothiophene. Then, Steglich esterification reaction was chosen for the formation of 1-(5-iodothiophen-2-yl)-4-(2-isopropyl-5-methylphenyl)butane-1,4-dione. For the formation of desired products (4A–C), Pd-catalysts Sonogashira coupling reaction was used. Secondly, the electrochemical anode catalyst performance of thymol hybrids 4A–C were investigated by using CV, CA, and EIS in hydrazine solution. The best performance was obtained from the hybrid 4C catalysts as $3.66 \text{ mA}\cdot\text{cm}^{-2}$ ($17.24 \text{ mA}\cdot\text{mg}^{-1}$ 4C). This study also improve that natural products may be alternative and environmentally friendly catalyst for the producing clean energy due to their electronic properties. As a result, thymol based new hybrids may be new anode catalyst for direct hydrazine fuel cell applications.

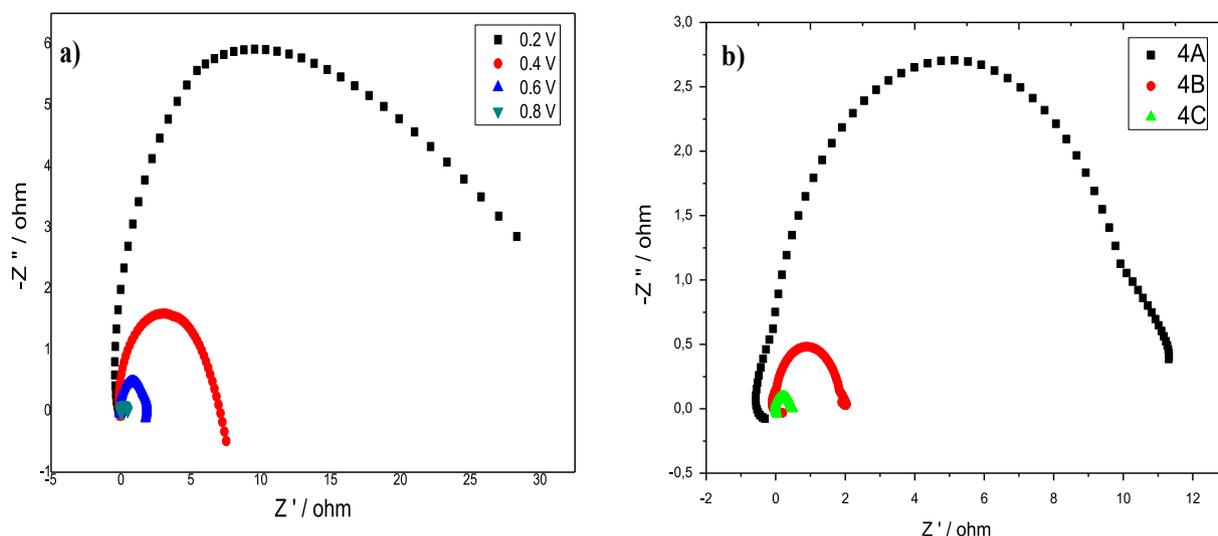


Fig. 7. EIS measurements of (a) hybrid 4C, (b) hybrid 4A, hybrid 4B and hybrid 4C.

CRedit authorship contribution statement

Kawa Hama Sharif: . **Hilal Kivrak:** Supervision, Validation. **Omrue Ozok-Arici:** . **Ayktu Caglar:** . **Arif Kivrak:** Supervision, Writing – original draft, Writing – review & editing.

Declaration of Competing 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.

Data availability

The authors do not have permission to share data.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2022.125597>.

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