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Investigation of the performance of *(4-(3-iodobenzo[b]thiophen-2-yl)-N,N-dimethyllaniline* as an anode catalyst for glucose electrooxidation

Omruye Ozok Arici[1*,] , Sefika Kaya[2], Aykut Caglar[3], Hilal Kivrak[2,4*], Arif Kivrak[3,5]

[1] Department of Biomedical Engineering, Faculty of Engineering and Architectural Sciences, Eskisehir Osmangazi University, Eskisehir, 26040, Turkey, omruye.ozok@ogu.edu.tr, ORCID: 0000-0002-4164-8650

[2]Department of Chemical Engineering, Faculty of Engineering and Architectural Sciences, Eskisehir Osmangazi University, Eskisehir, 26040, Turkey, sefikakaya@ogu.edu..tr, ORCID: 0000-0003-3556-6461

[3]Technology and Innovation Center, Advance Organic Synthesis Laboratory, Eskisehir Osmangazi University, Eskişehir 26040, Turkey, aykut_802@hotmail.com, ORCID: 0000-0001-0681-1096

[4]Translational Medicine Research and Clinical Center, Eskisehir Osmangazi University, 26040 Eskisehir, Turkey, hilaldemir.kivrak@ogu.edu.tr, ORCID: 0000-0001-8001-7854

[5]Department of Chemistry, Faculty of Sciences, Eskisehir Osmangazi University, 26040 Eskisehir, Turkey, arif.kivrak@ogu.edu.tr , ORCID: 0000-0003-4770-2686

ABSTRACT

In this study (4-(3-iodobenzo[b]thiophen-2-yl)-N,N-dimethyllaniline (4), Sonagashira Coupling Reaction was synthesized using Electrophilic Cyclization Reactions. Then, the anode catalyst performance for glucose electrooxidation was investigated. The electrocatalytic activities of the organic catalyst were investigated by CV, CA and EIS measurements in 1 M KOH + 0.5 M $C_6H_{12}O_6$ solution. Interestingly, electrochemical depositing on organic catalyst by Pd metal increased the specific activity, and it was calculated as 0.61 mA/cm^2 Consequently, Pd@4 catalyst will be used as an electrocatalyst with high specific and stability and low charge transfer activity.

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Corresponding author

1. Introduction

Energy is one of the most important factors for nature and social life. Energy production, conversion and consumption are considered as an important factor for the environment and a sustainable life. Technological developments, industrialization and the increase in the world population increase the demand for energy day by day [1]. With energy systems, environmental damage occurs in the stages from energy production to consumption and disposal.

Recently, important solutions have been developed for the current environmental problems associated with the release of substances harmful to the environment and human health. Among these solutions, renewable energy sources take an important place as an alternative [2]. Recently, among the renewable energy sources, batteries [3], organic solar cells [4], and fuel cells [5], stand out as clean energy sources. glucose [6], hydrazine [7], formic acid [8] and methanol [9] are often used in fuel cells. The direct use of glucose in fuel cells is one of the most popular methods due to its advantages [10]. Glucose is the most abundant natural monosaccharide and has a high energy density, making it a toxic, explosive and non-volatile organic molecule [11]. When a glucose molecule is completely oxidized, it forms 24 e$^-$ and non-toxic products carbon dioxide and water (CO_2 and H_2O) [12]. Glucose electro-oxidation reactions in alkaline medium are shown below:

Anode: $C_6H_{12}O_6+36OH^- \longrightarrow 6CO_3^{2-} + 24H_2O + 24e^-$ (1)

Cathode: $6O_2+24e^- +12\ H_2O \longrightarrow 24OH^-$ (2)

Overall: $C_6H_{12}O_6 + 6O_2 + 12OH^- \longrightarrow 6CO_3^{2-} + 12\ H_2O$ (3)

Recently, many researchers have been working on the oxidation of glucose using anode electrocatalysts. Chai et al. found that Pd/C, Pd_3Cu/C and Pd_3Cu-B/C electrocatalysts and Pd_3Cu-B/C catalyst prepared by a simple aqueous phase approach exhibited the best stability and higher activity in glucose electrooxidation [13]. Yan et al. found that Pd_xAu_y/C exhibits a very sensitive and linear amperometric response for glucose molecules [14]. In addition, Basu et al. reported that Au/C and Pt-Au/C catalysts were tested in the glucose electrooxidation reaction and the Pt-Au/C catalyst showed more activity than the Au/C catalyst and showed lower activity than Pt/C[15].

Heterocyclic compounds such as thiophenes, indoles, pyridines are of vital importance for materials science as well as their biological activities[16]. Benzothiophene derivatives are among the most well-known heteroaromatic compounds. Organic molecules have advantages such as greater flexibility, lower molecular weight and wide absorption bands[17]. For this reason, organic catalysts are used for clean energy.

In this study, we aimed to develop glucose electrooxidation reaction organic-based catalysts to reduce the high cost of anode catalysts due to the high cost of noble metals. (4-(3-iodobenzo[b]thiophen-2-yl)-N,N-dimethyllanilin was synthesized as anode catalysts for the glucose electrooxidation reaction. All designed benzothiophene derives were defined by using ^{1}H NMR, and ^{13}C NMR. After characterization, the electro-oxidation activity of glucose as the anode catalyst of this organic catalyst was investigated. Glucose electrooxidation activities were found by CV, CA and EIS analyses. In addition, Pd metal was electrodeposited on the benzothiophene derivative to explore the effects of electrochemical activity. A-Pd-doped organic catalyst (Pd-4A) was characterized using electron microscopy with energy dispersive x-ray (SEM-EDX). Pd-Organic catalyst systems could be promising to work as fuel cell anode catalysts.

2. Experimental measurement

2.1. Preparation of organic catalysts

Synthesis of N,N-dimethyl-4-((2-(methylthio)phenyl)ethinyl)aniline (3)

2-Iodothianisole (1) (1 equiv.), $PdCl_2(PPh_3)_2$ (0.05 equiv.), 4-ethinyl-N,N-dimethylaniline (2) (1.2 equiv.) and CuI (0,05 equiv.) in THF (10 mL) and triethylamine (15 mL) were mixed at room temperature for 24 hours. When starting compound was gone, the mixture was extracted with EtOAc (3 X 15 mL). The organic phase was dried with $MgSO_4$, filtrated and concentrated under reduced pressure. The residue purified by using flash column chromatography on silica gel Hexane/Ethyl acetate (100:1) to give N,N-dimethyl-4-((2-(methylthio)phenyl)ethinyl)aniline (3) (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 9 Hz, 3H), 7.31-7.21 (m, 1H), 7.16 (dd, *J* = 8;1 Hz, 1H), 7.12-7.03(m, 1H), 6.67 (d, *J* = 8 Hz, 2H), 2.99(s, 6H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 140.9, 132.7, 131.8, 127.9, 124.2, 124.1, 122.3, 111.8, 97.2, 40.2, 15.1.

Synthesis of (4-(3-iodobenzo[b]thiophen-2-yl)-N,N-dimethyllaniline (4)

N,N-dimethyl-4-((2-(methylthio)phenyl)ethinyl)aniline (3) (1 equiv.) in dichloromethane (30 mL) was added molecular iodide (2 equiv.) at room temperature. After 2 hours, reaction mixture was washed with saturated $Na_2S_2O_3$ and extracted with dichloromethane (3 X 20 mL). The combine organic phase was dried with $MgSO_4$, filtrated and concantrated under reduced pressure. The residue purified by using flash column chromatography on silica gel Hexane/Ethyl acetate (100:1) to give (4-(3-iodobenzo[b]thiophen-2-yl)-N,N-dimethyllaniline (4) (96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8; 0.5 Hz, 1H), 7.76(d, *J* = 8 Hz, 1H), 7.63(d, *J* = 8 Hz, 2H), 7.47-7.43 (m, 1H), 6.82(d, *J* = 8 Hz, 2H), 3.01(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 150.6, 142.9, 142.1, 138.6, 130.8, 125.86, 125.2, 124.9, 121.9, 111.8, 76.7, 40.2.

2.2. Electrochemical measurements

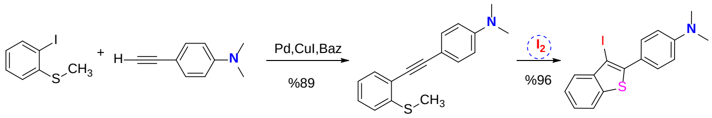
Electrochemical measurements were performed using 1 M KOH + 1 M Glucose solution, using cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) methods. CV measurements were carried in the potential range of -0.6-0.8 V, scanning speed of 50 mV/s. In order to increase the electrochemical activity of the catalyst, Pd metal was deposited on the benzothiophene derivative by electrodeposition method. Palladium metal was deposited on organic structure with CV in 0.1 mM K_2PdCl_4 + 0.1 M H_2SO_4 + 0.2 mM HCl solution at 10 mV/s scan rate. CA measurements were applied at potentials of -0.4, -0.2, 0, 0.2 and 0.4 V to determine the stability of the catalysts in 1000 s. The resistance of the catalyst to glucose electrooxidation was determined by EIS measurements at different values ranging from -0.6 to 0.4 V.

3.Results and discussion

3.1. Synthesis

The Sonogashira coupling reaction is an important reaction in organic chemistry that allows Pd-catalyzed formation of new carbon-carbon bonds between primary alkynes and halogenated aromatic structures [18]. In the first step of the study, a new carbon-carbon bond was established with the Sonagashira coupling reaction with 4-ethinyl-N,N-dimethylaniline catalyzed by 2 iodothioanisole Pd and N,N-dimethyl-4-((2-(methylthio)phenyl)ethinyl)aniline with 89%

yield. (3) synthesized. In the next step, (4-(3-iodobenzo[b]thiophen-2-yl)-N,N-dimethyllaniline (4) was synthesized in a high yield of 96% by electrophilic cyclization reaction(Fıgure 1).

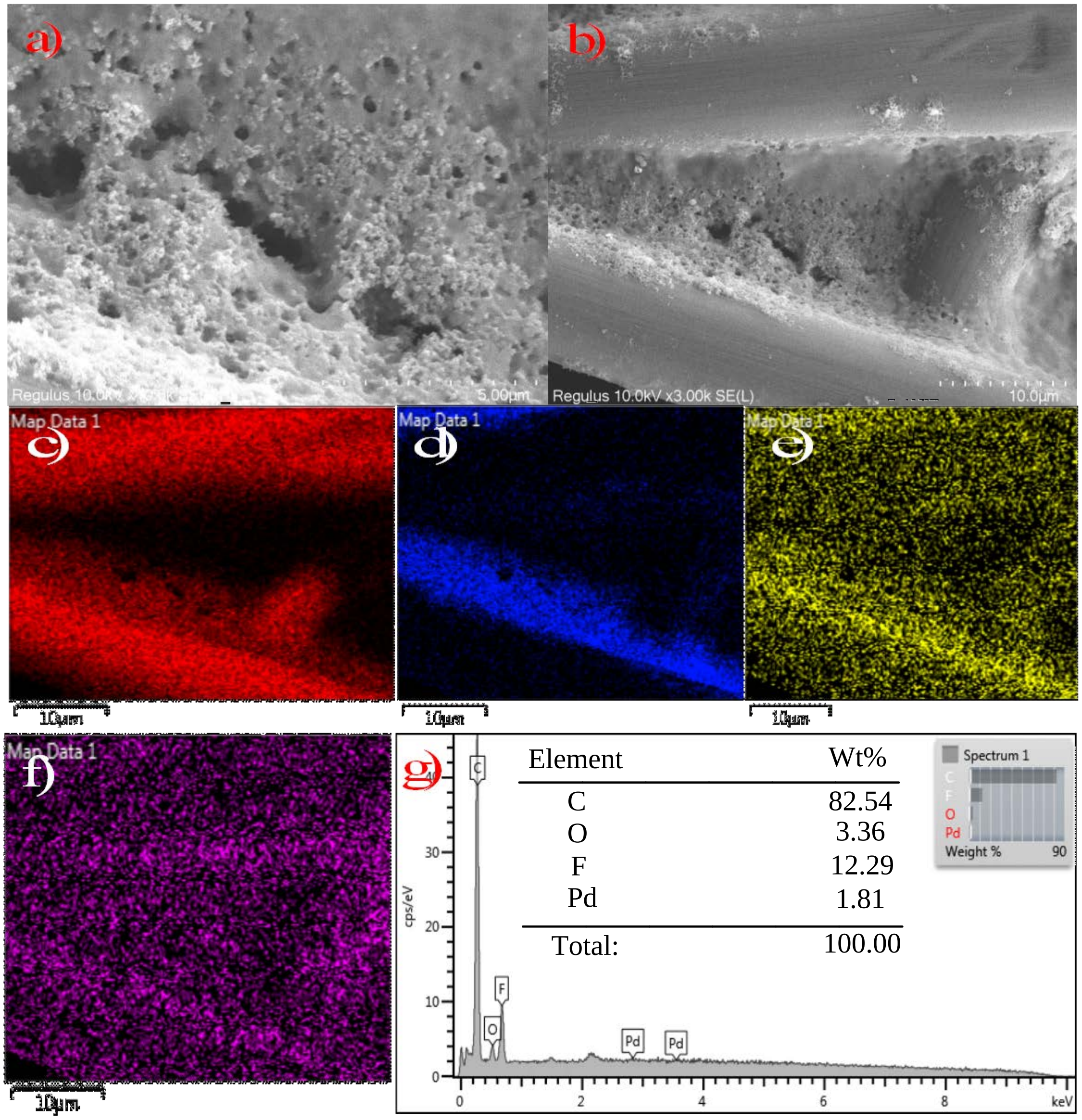


1 2 3 4

Fıgure 1. Synthesis of 4-(3-iodobenzo[b]thiophen-2-yl)-N,N-dimethyllaniline

3.2.Characterization Results

Figure 2 indicates the SEM-EDX and mapping analysis obtained to examine the surface structure and morphology of the **4** catalyst. As can be seen from the SEM images, it was observed that agglomeration did not occur and a homogeneous distribution occurred. Mapping and EDX analyses demonstrate that C (red), F (blue), O (yellow), and Pd (purple) elements are formed. These results show that the electrochemically Pd coating on the organic material has taken place. The electrochemical characterization results are evidence that the changed activity after Pd coating is due to the Pd atoms formed on the surface.

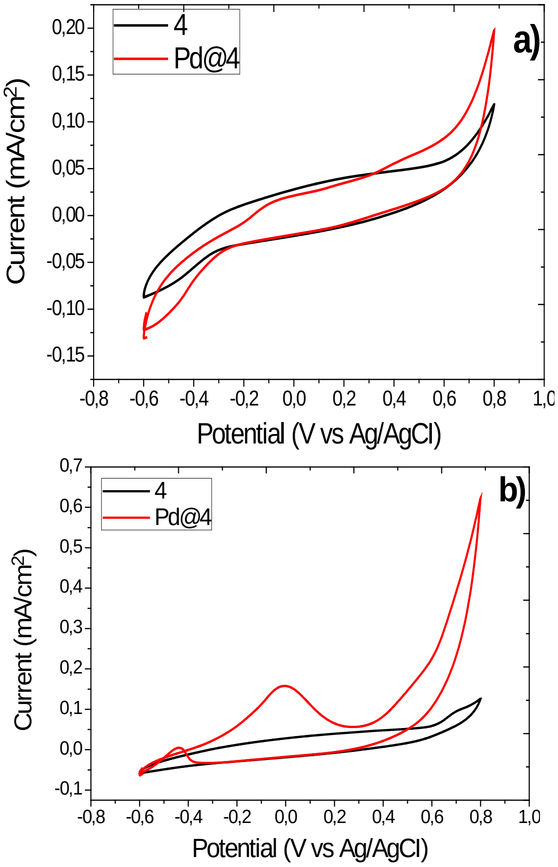


Element	Wt%
C	82.54
O	3.36
F	12.29
Pd	1.81
Total:	100.00

Figure 2. *SEM (a, b)-EDX (g) and mapping (C (c), F (d), O (e), and Pd (f)) of **4** catalyst*.

3.3. Electrochemical results

Glucose electrooxidation activities of **4** and **Pd@4** organic-based catalysts were investigated by CV measurements in 1 M KOH + 1 M $C_6H_{12}O_6$ solution. The CV analyses of the organic-based catalysts in the potential range of -0.6 ~ 0.8 V were presented in Figure 3. Although glucose is a high-energy fuel, it is difficult to break down, so no oxidation peak was observed in the glucose electrooxidation results of the organic catalyst. [19]. When the organic catalyst was doped with active metal such as Pd, the oxidation peak was observed as can be seen in Figure 3b. According to the EDX analysis (Figure 2g) results, it was observed that Pd metal was doped with organic material, albeit in a small amount. Therefore, the glucose oxidation peak current density occurring at a potential of 0.0 V (Figure 3b) was obtained as approximately 0.17 mA/cm^2.



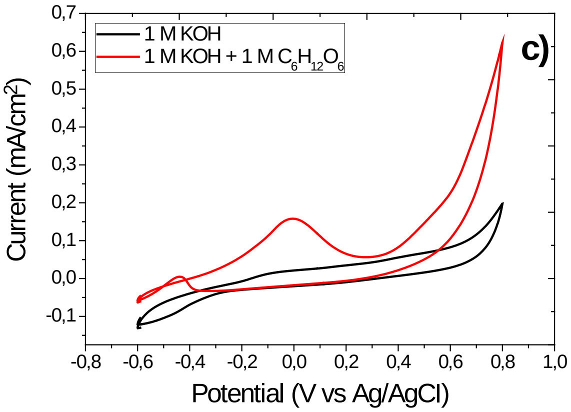


Figure 3. *CV analyses of **4** and **Pd@4** organic-based catalysts at a scan rate of 50 mV/s **a)** 1 M KOH, **b)** 1 M KOH + 1 M* $C_6H_{12}O_6$*, and c) comparison of Pd@4 organic-based catalyst in 1 M KOH and 1 M KOH + 1 M* $C_6H_{12}O_6$ *solutions.*

Figure 4 demonstrates the CA curves of organic-based catalysts. Firstly, CA curves of **Pd@4** organic-based catalyst at different potentials (-0.4 V to 0.4 V) were obtained (Figure 4a). The best stability was 0.4 V potential after 1000 s. As can be seen from Figure 4b, **Pd@4** organic-based catalyst exhibited the best catalytic activity and stability compared to the **4**, as in CV results.

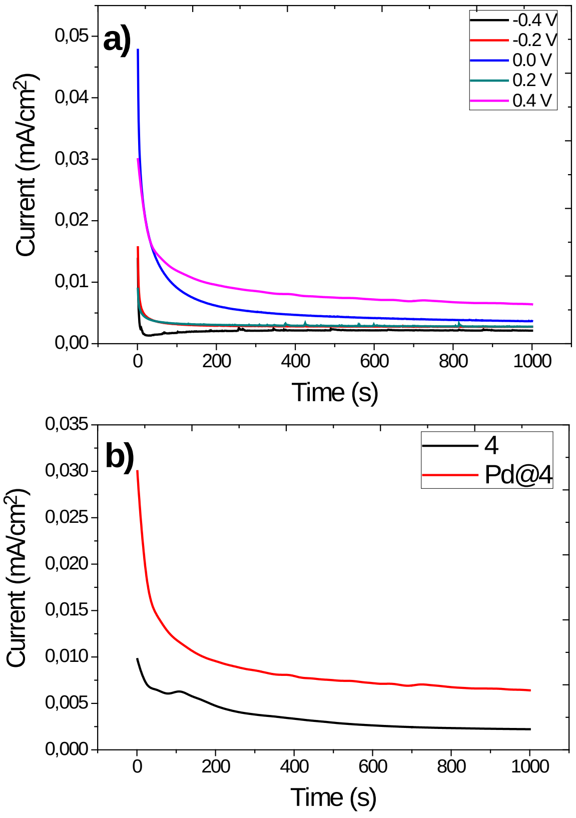


Figure 4. *CA curves of **a) Pd@4** organic-based catalyst at different potentials and **b)** comparison of organic-based catalysts at 0.4 V potential in 1 M KOH + 1 M* $C_6H_{12}O_6$ *solution.*

Nyquist plots obtained from EIS analysis were realized to investigate the electrochemical resistance of organic-based catalysts. In Nyquist diagrams, as the diameter of the semicircle decreases, the charge transfer resistance decreases and therefore the electrocatalytic activity increases. [20-21] Nyquist plots performed in 1 M KOH + 1 M $C_6H_{12}O_6$ solution was given in Figure 5(a, b). Nyquist plots were first obtained with **Pd@4** organic-based catalyst at different potentials (Figure 5a). As in the CA analysis, it showed the best electrochemical resistance of 0.4 V potential. The **Pd@4** organic-based catalyst exhibited the best resistance compared to the **4** at 0.4 V potential (Figure 8b).

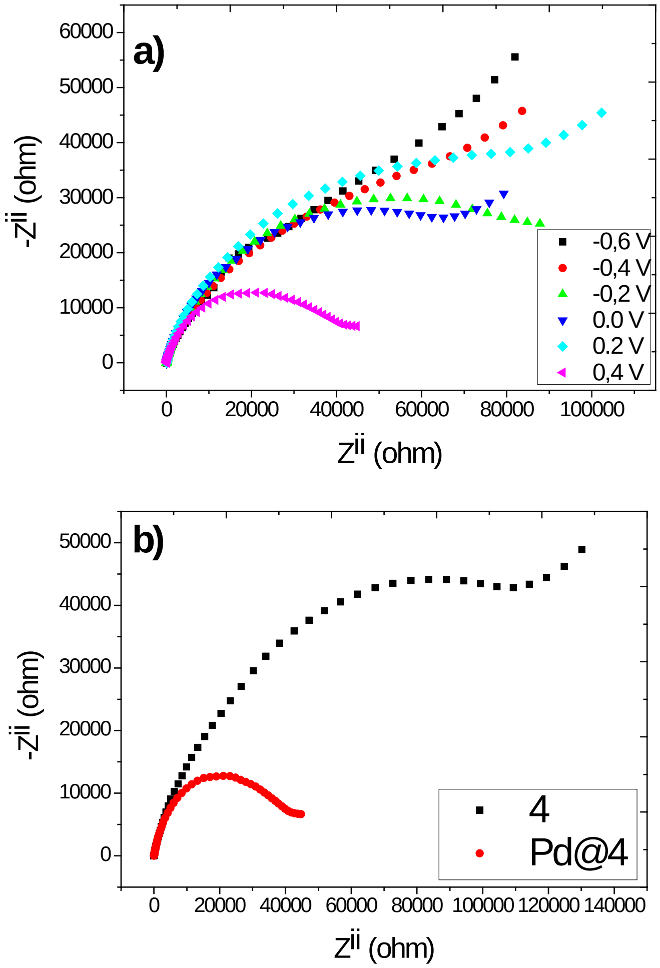


Figure 5. *Nyguist plots of **a) Pd@4** organic-based catalyst at different potentials and **b)** comparison of organic-based catalysts at 0.4 V potential in 1 M KOH + 1 M $C_6H_{12}O_6$ solution.*

4. Conclusion

In this study, (4-(3-iodobenzo[b]thiophen-2-yl)-N,N-dimethyllaniline (4) catalyst was synthesized via Sonogashira coupling reaction and electrophilic cyclization reactions. Then, the anode catalyst performance for glucose electrooxidation was investigated. The electrocatalytic activities of the organic catalyst were investigated by CV, CA and EIS measurements in 1 M KOH + 0.5 M $C_6H_{12}O_6$ solution. Interestingly, electrochemical depositing on organic catalyst by Pd metal increased the specific activity, and it was calculated as 0.61 mA/cm^2. The SEM-EDX results of Pd@4 confirmed the successful deposition of Pd metal on the organic catalyst. Consequently, Pd@4 catalyst will be used as an electrocatalyst with high specific activity and stability and low charge transfer resistance.

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