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Development and application of bimetallic catalysts supported carbon nanotube for 1-propanol electrooxidation

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ABSTRACT

Herein, carbon nanotube supported bimetallic catalysts (PtBi/CNT) are synthesized at various metals weight loadings by $NaBH_4$ reduction method. The surface morphology and crystal structure of the catalysts are investigated via X-ray diffraction (XRD) and electron microscopy with energy dispersive X-ray (SEM-EDX) advance surface methods. According to XRD results, the crystal size of PtBi(90:10)/CNT catalyst is determined as 4.66 nm. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronoamperometry (CA) electrochemical techniques are used to determine 1-propanol electrooxidation activities of the catalysts. The highest specific activity and mass activity are obtained with PtBi(90:10)/CNT catalyst as 5.663 mA/cm^2 and 447.21 mA/mg Pt, respectively. However, it is concluded that PtBi(90:10)/CNT catalyst can be used as an anode catalyst in 1-propanol electrooxidation with long-term stability and low resistance.

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1. Introduction

In recent years, the increasing world population, the increase in energy demand, the depletion of fossil fuels and the damage to the environment have led to the search for renewable energy sources [1-4]. In this context, fuel cells come to the fore with their zero gas emission, high energy efficiency, sustainability and environmental friendliness [5-7]. Fuel cells are devices that convert chemical energy into electrical energy by electrochemical reactions in the presence of a fuel and an oxidizer [8]. Although hydrogen is a clean and efficient fuel for fuel cell, there are problems such as producing, transporting and storing pure hydrogen [9]. These problems have led research to liquid fuels such as alcohol. Alcohols with high energy density are easy to transport and process [10, 11]. Direct alcohol fuel cells work in both acidic and alkaline environments. However, the oxidation reaction is slow in acidic environment. The alkaline medium, where the oxidation reaction is faster and the corrosive effect is less, is more preferred [12-14]. 1-propanol is a three-carbon alcohol and 18 electrons are produced as a result of the complete oxidation reaction (Eq. 1)[15]. Compared to other alcohols, it has superior properties such as being less toxic and having a higher energy density [16, 17]. However, it is a cheap renewable fuel source that can be produced from biomass [18].

$$C_3H_7OH + 5H_2O \rightarrow 3CO_2 + 18H^+ + 18e^- \quad (1)$$

Nobel metals (e.g., Pt, Pd, Ru) and their alloys have been frequently investigated as anode and cathode catalysts in fuel cell technology. Monometallic catalysts have superior physicochemical properties. However, bimetallic catalysts overcome the disadvantages of monometallic catalysts such as electrode poisoning and are more active [19, 20]. In addition, carbon-based materials with a large surface area and porous structure, which provide homogeneous dispersion of the catalyst, increase the catalytic activity, are preferred as support materials [21-23]. Carbon nanotubes (CNTs), one of the carbon-based materials, come to the fore in scientific studies with their high electrical conductivity, mechanical and thermal stability, large surface area and porosity [24, 25]. Etesami et al. prepared monometallic and bimetallic catalysts of Pt, Pd, and Au metals with pencil graphite support material for 1-propanol electrooxidation and compared catalytic activity of the catalyst in alkaline and acidic media. They reported that bimetallic catalysts have higher catalytic activity in alkaline media [19]. Kim et al. synthesized carbon supported monometallic and bimetallic catalysts at different atomic ratios of Pt and Sn. They emphasized that the addition of Sn metal to Pt/C catalyst reduces electrode poisoning and improves catalytic activity [26]. Synthesized Pt/RuO_2 catalyst was used to investigation 1-propanol electrooxidation activity by Spasojevic et al. They also declared that the increase in RuO_2 content increased the catalytic activity [27]. The different catalyst such as PdSn, PdRu, and PdIr [28], PtRh [29], PtAu/Ni [30], Pt/PANI/Au [31] were used for 1-propanol electrooxidation in literature.

In this study, 1-propanol electrocatalytic performances of bimetallic catalysts were investigated. The bimetallic

catalysts were synthesized at various Pt and Bi metals weight loadings by $NaBH_4$ reduction method. CV, EIS and CA electrochemical measurements were used to determine catalytic activities of the catalysts. The surface structure and crystal size of the catalysts were determined with SEM-EDX and XRD analyzes.

2. Experimental

2.1. Synthesis and characterization

Pt/CNT, Bi/CNT, and PtBi/CNT at different atomic ratios were prepared with $NaBH_4$ reduction method. The loaded metal was adjusted as 10 wt% on a support material (CNT). Precursor metal salts (Cl_6K_2Pt and $Bi(NO_3)_3.5H_2O$) were weighed and dissolved in pure water. After adding support material, prepared solution was stirred during 2 h. The $NaBH_4$ was added into the solution by dropwise. The solution was stirred for 1 h, filtered, washed and then dried in vacuum oven. Advanced surface characterization techniques such as SEM-EDX (Zeiss Sigma 300) and XRD (Panalytical Empyrean) were applied to determine the characterization of the catalysts.

2.2. Electrochemical measurements

CHI 660E potentiostat device with three electrode system was used for CV, CA, and EIS analyzes. The three-electrode system consisted of glassy carbon as working electrode, Pt wire as counter electrode, and Ag/AgCl as reference electrode. All electrochemical experiments were taken in 1 M KOH + 1 M 1-propanol solution. The 1-propanol electrooxidation activities of the catalyst were investigated by CV at -1.0-0.6 potential range V and 50 mV/s. The stability of the catalysts was defined with CA analyzes at -0.6, -0.4, -0.2, 0.0, and 0.2 V in 1000 s. EIS measurements were performed at different potential values (from -0.6 V to 0.2 V) in 300 kHz-0.04 Hz frequency range.

3. Results and Discussion

3.1. Physical characterization

The crystallinity of the Pt/CNT and PtBi(90:10)/CNT catalysts were determined with XRD analysis. Figure 1 presented the XRD patterns of the catalysts. Accordingly, the C (002) plane related hexagonal carbon structure was observed at 25.7° diffraction peak point [32]. The (111), (200), (220), and (311) planes were appeared at around 43.1°, 53.1°, 67.0°, and 78.5° belonging the face-centered cubic (fcc) Pt structure, respectively [33]. A positive shift was observed in the same Pt peaks for the PtBi(90:10)/CNT catalyst. The (112) planes of the Bi diffraction peak for the PtBi(90:10)/CNT catalyst was observed at 39.9° [34]. The crystal size of Pt/CNT and PtBi(90:10)/CNT catalysts were calculated by using Scherrer's equation and were found to be 2.81 nm and 4.66 nm, respectively.

The surface formation of PtBi(90:10)/CNT catalyst was explained via SEM-EDX analysis. SEM-EDX results of the catalyst are shown in Figure 2. In SEM images, it was observed that the metals were homogeneously dispersed without clumping. In addition, the EDX spectrum of the catalyst included peaks of Pt and Bi structures.

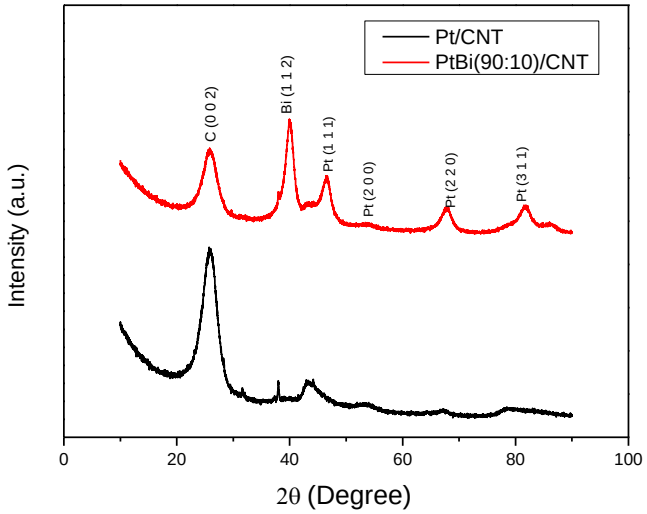
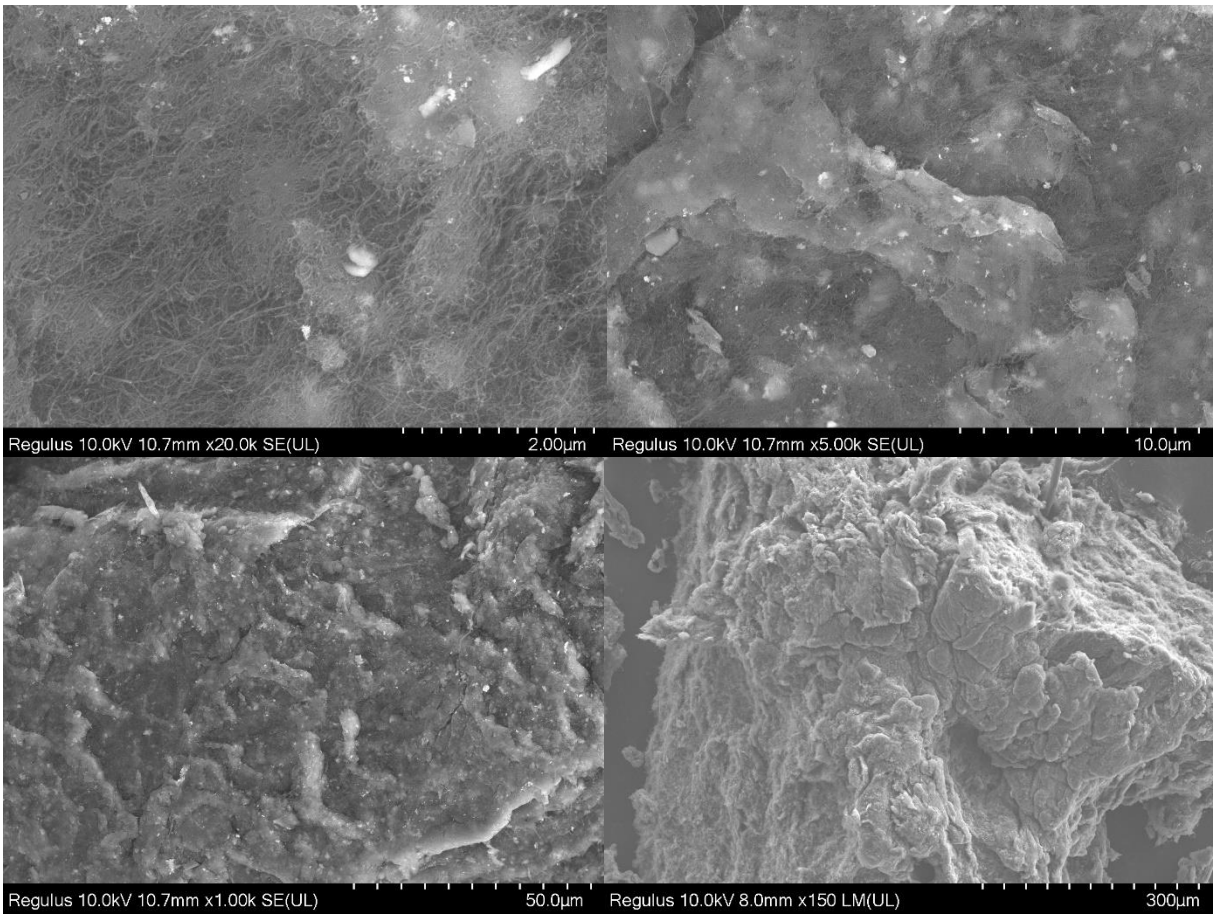


Figure 1. *XRD patterns of the Pt/CNT and PtBi(90:10)/CNT catalysts.*



Element	Wt%
C	80.49
O	3.56
Pt	15.32
Bi	0.63
Total:	100.00

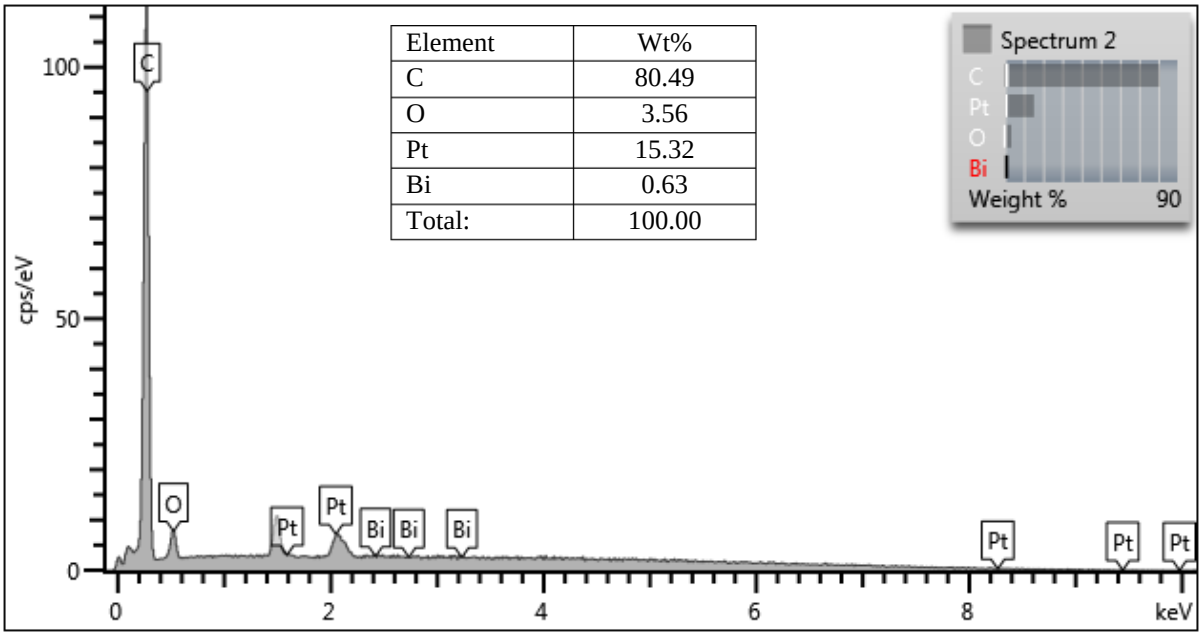


Figure 2. *SEM-EDX results of PtBi(90:10)/CNT catalyst.*

3.2. Electrochemical results

1-propanol electrooxidation performance of Pt/CNT, Bi/CNT, and PtBi/CNT at different atomic ratios were determined with CV measurements. The CV measurements were applied in 1 M KOH + 1 M 1-propanol solution in the potential range of -1.0 - 0.6 V. The obtained CV results are shown in Figure 3. In Figure 3, two characteristic peaks were observed between the potentials of -0.6 to 0.1 V in the forward scan and -0.5 to -0.2 V in the reverse scan. The observed peaks in the forward scan indicate 1-propanol oxidation. Table 1 includes the electrochemical properties of catalysts for 1-propanol electrooxidation. As the Pd metal ratio increased, the current value increased and the PdBi(90:10)/CNT catalyst showed the highest specific activity with 5.663 mA/cm^2 value.

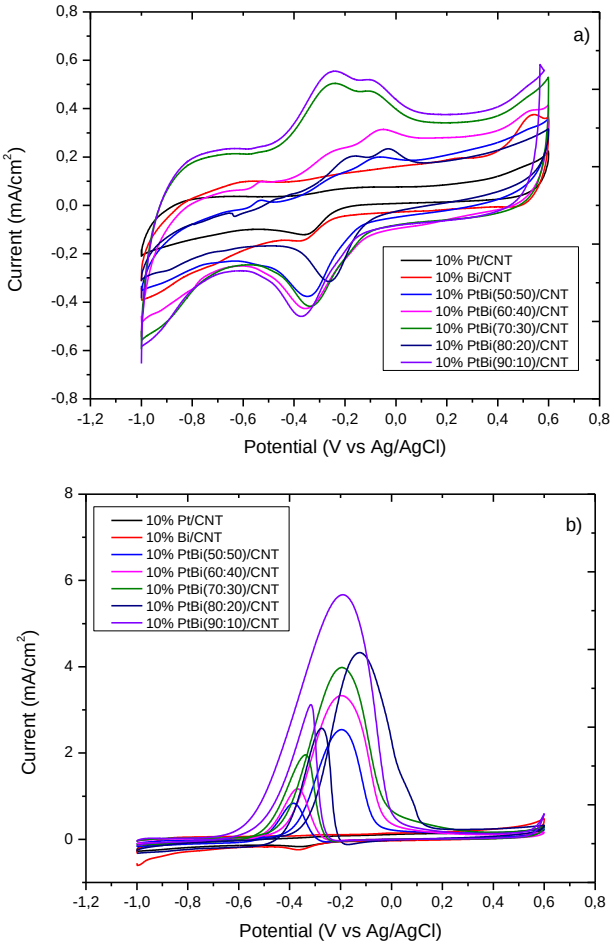


Figure 3. *CV curves of 10% Pt/CNT, 10% Bi/CNT, and 10% PtBi/CNT at various atomic ratios in (a) 1 M KOH (b) 1 M KOH + 1 M 1-propanol.*

CA measurements were applied to determine the stability of the 10% PtBi(90:10)/CNT catalyst at different potentials in 1000 s. The CA curves of the catalyst were shown in Figure 4. As seen in the Figure 4, there was a decrease at the beginning of the measurements as a result of electrode poisoning of intermediate species formed during electrooxidation. The catalyst was provided the highest catalytic activity and longest stability at -0.6 V potential.

The catalytic resistance of 10% PtBi(90:10)/CNT catalyst was explained by using Nyquist curves (Figure 5). Nyquist curves obtained with EIS measurements are usually semicircular. Since the diameter of the semicircle is proportional to the charge transfer resistance (R_{ct}), the smaller the diameter, the higher the catalytic activity [35, 36]. For 10% PtBi(90:10)/CNT catalyst, the best catalytic activity and lowest charge transfer resistance were provided at -0.2 V.

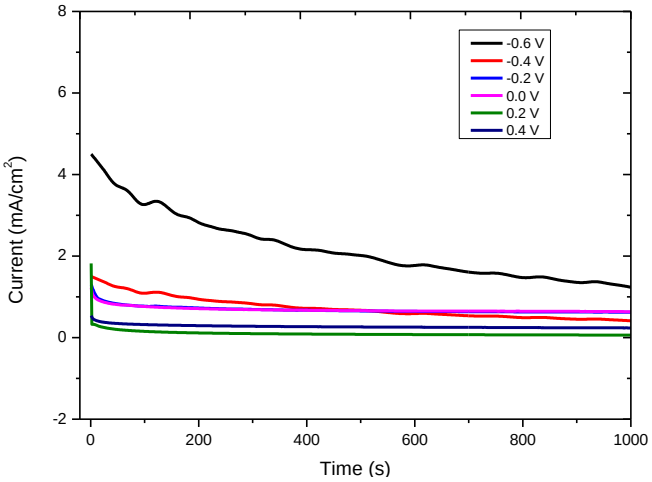


Figure 4. *CA curves of 10% PtBi(90:10)/CNT catalyst at different potentials.*

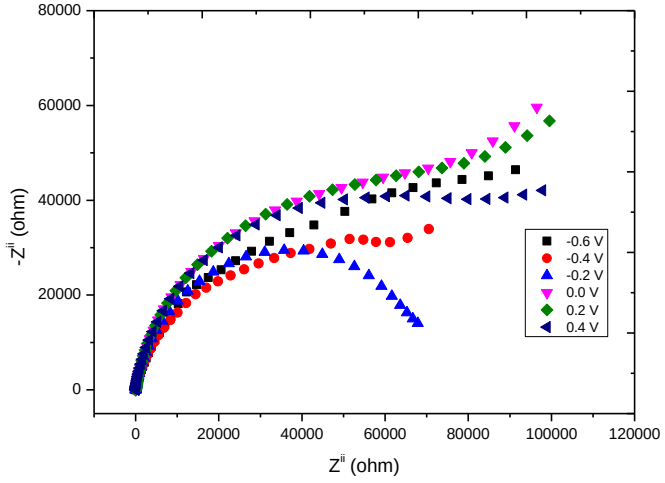


Figure 5. *EIS profile of 10% PtBi(90:10)/CNT catalyst at different potentials.*

Table 1. *The electrochemical properties of catalysts for 1-propanol electrooxidation.*

Catalyst	Current, mA/cm^2	Peak Potential, V	Onset Potential, V	Mass Activity, mA/mg Pt
10% PtBi(50:50)/CNT	2.535	-0.199	-0.500	218.90
10% PtBi(60:40)/CNT	3.330	-0.196	-0.504	280.07
10% PtBi(70:30)/CNT	3.974	-0.196	-0.505	330.05
10% PtBi(80:20)/CNT	4.316	-0.124	-0.507	347.61
10% PtBi(90:10)/CNT	5.663	-0.189	-0.672	447.21

4. Conclusion

In this study, CNT supported bimetallic catalysts were prepared at different Pt and Bi metal ratios by using $NaBH_4$ reduction method. The synthesized catalysts were characterized via XRD and SEM-EDX characterization methods. CV, EIS, and CA electrochemical techniques were applied to determine the 1-propanol electrocatalytic activities of the catalysts. The following results were obtained from 1-propanol electrooxidation measurements and characterization results:

- The crystal size of PtBi/CNT catalyst from XRD results was found as 4.66 nm.
- In SEM images, it was observed that the metals were homogeneously dispersed without clumping.
- PtBi(90:10)/CNT catalyst exhibited the best catalytic activity and mass activity as 5.663 mA/cm^2 and 447.21 mA/mg Pt, respectively. This result can be explained by the synergistic effect between Pt and Bi metals.
- According to CA and EIS results, compared to other catalysts, PtBi(90:10)/CNT had the lowest long-term stability and lowest resistance in the 1-propanol electrooxidation reaction.
- PtBi(90:10)/CNT catalyst is promising as anode catalysts for 1-propanol fuel cells.

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