

## The Effects of Calcination Temperature of Nickel Supported on Candle Soot towards Ethanol Oxidation Reaction (EOR)

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### ABSTRACT

The discovery of cost-effective electrocatalyst materials suitable for anode catalyst for direct ethanol fuel cell (DEFC) is a significant problem. In this context, candle soot has been selected as a catalyst support material as it has higher electrical conductivity. Furthermore, there is a limited amount of research conducted on the use of candle soot as a catalyst support, making it an interesting and novel avenue of exploration. The purposes conducting this research was to evaluate the electrochemical properties of different calcination temperature supported on candle soot towards ethanol oxidation reaction (EOR). Ni/FS electrocatalyst were calcined at 600, 650, 700, 750, and 800 °C. Chronoamperometry (CA) and cyclic voltammetry (CV) methods were used to analyze the electrochemical characteristics. CV investigation showed that Ni/FS catalytic activity has the maximum current density of 6.93 mA/cm<sup>2</sup> at 800 °C. 800 °C had the greatest I<sub>F</sub>/I<sub>B</sub> ratio (1.15) among the calcination temperatures. CA research showed that 800 °C Ni/FS, supported by candle soot, had the highest retention rate (50.00 %) and was the most stable electrocatalyst. Hence, 800 °C of calcination temperature is the maximum temperature for nickel supported on candle soot towards ethanol oxidation reaction.

#### Keywords:

Calcination temperature, nickel, candle soot, ethanol oxidation reaction

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### 1. Introduction

Direct ethanol fuel cells (DEFCs) have garnered significant interest in recent years due to their ability to convert chemical energy into electricity. This is attributed to their notable efficiency and

eco-friendly. Ethanol, with a high energy value of  $29.7 \text{ kJ g}^{-1}$ , is widely recognized as an affordable and sustainable biofuel option [9]. It may be utilized as a gasoline addition, offering the benefits of decreasing carbon monoxide emissions, facilitating liquid fuel storage, exhibiting minimal toxicity, and possessing a higher theoretical energy density compared to hydrogen fuel [2]. Ethanol is considered a promising alternative fuel; however, its electrooxidation process is intricate and presents challenges, including reduced energy efficiency in fuel cells and the high cost of Pt-based catalysts. The development of a cost-effective and high-performing anode catalyst would offer a potential solution to the aforementioned challenges. Nickel and nickel-based catalysts are regarded as highly desirable candidates. Nickel is considered to be a cost-effective element and has a strong affinity for oxygen, making it an oxyphilic element. The presence of nickel on the catalyst can augment the  $\text{OH}_{\text{ad}}$  species and facilitate the provision of  $\text{OH}_{\text{ad}}$  at a low potential. This, in turn, enables the oxidative desorption of intermediates, leading to enhanced activity in the ethanol oxidation reaction (EOR) [6,7]. Nevertheless, the insufficient conductivity and limited active sites of nickel continue to be significant drawbacks in its practical use.

Therefore, the utilization of nickel metals in conjunction with conductive materials, such as carbon-based materials, as catalysts, is seen as a crucial approach for enhancing both electrical conductivity and surface area for the active sites. Carbon-based supports, which includes carbon black, mesoporous carbon [1], activated carbon, carbon [11], and graphene [3]. Candle soot is regarded as one of the most promising catalyst support, as it has the low cost, high electrical conductivity, and large surface area [4,8]. These properties will result in an increased number of active sites and enhanced stability, hence promoting electrocatalytic activities.

Besides that, the study of synthesis conditions for materials is of utmost importance due to its substantial impact on the structural characteristics and electrochemical properties of those materials, ultimately influencing their overall electrochemical performance. This study presents a novel non-precious catalyst for the ethanol oxidation reaction (EOR), which involves the utilization of candle soot supported on nickel produced by the wet impregnation method. The impact of varying calcination temperatures on the electrochemical characteristics and performance of the materials was thoroughly examined by cyclic voltammetry (CV) and chronoamperometry (CA) characterization techniques.

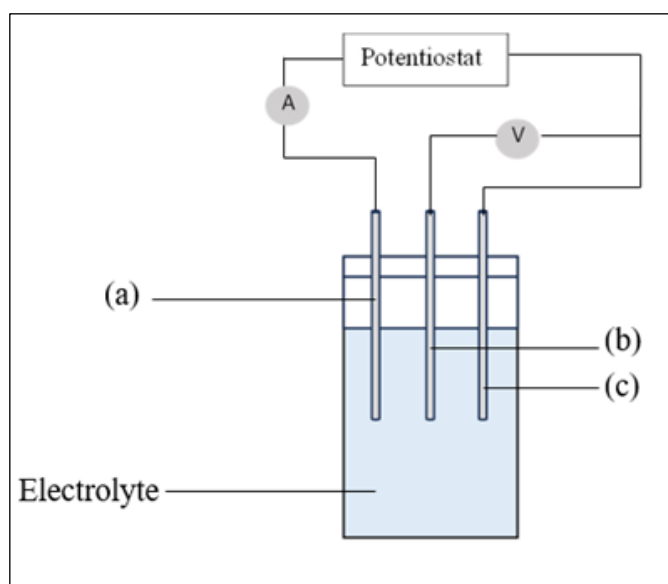
## 2. Materials and Methods

### 2.1 Preparation of Ni/FS Electrocatalyst

The electrocatalyst was prepared in three stages: (i) collecting candle soot nanoparticles, (ii) preparing functionalized candle soot (FS) [12], and (iii) synthesizing Ni/FS. Approximately, 2 g of soot was collected from the tip of the paraffin candle. The collected soot was sonicated at 37 kHz and 100 W for 5 minutes with ethanol and DI water in a 1:1 ratio. Next, washed soot (WS) dried overnight at  $110 \text{ }^\circ\text{C}$  to completely remove the excess moisture from the soot. After that, WS was functionalized with  $\text{HNO}_3$ . The FS dried in the oven for 12 hours at  $60 \text{ }^\circ\text{C}$  to eliminate moisture from soot particles. 200 mL of DI water was used to dissolve the FS powder. The precursor of aqueous Ni  $(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  was added to the mixture. The mixture was heated at  $90 \text{ }^\circ\text{C}$ . The paste was dried in a  $110 \text{ }^\circ\text{C}$  oven overnight before the sample was calcined in the furnace surrounded by an Argon gas flow to create Ni/FS electrocatalyst. Ni/FS is synthesized under varying high temperatures ranging from  $600$  to  $800 \text{ }^\circ\text{C}$ .

## 2.2 Characterization of Ni/FS Electrocatalyst

The crystalline structure was determined using x-ray diffraction (XRD) on a Bruker AXS DB Advance diffractometer (CuK $\alpha$  radiation,  $\lambda = 0.154$  nm) ranges from 30° to 80°. Then, Ni/FS electrocatalysts were tested for their electrochemical properties using cyclic voltammetry (CV) and chronoamperometry (CA) using potentiostat, VersaSTAT 3. A three-electrode cell configuration was utilized in the experiment, where the reference electrode consisted of Ag/AgCl immersed in a 3 M KCl solution. The counter electrode was composed of Pt wire, while the working electrode was a Ni/FS modified glassy carbon electrode (GCE) with a geometric area of 0.07068 cm<sup>2</sup>. Before analysis, the catalyst ink for the working electrode was prepared. 10 mg of Ni/FS electrocatalyst was mixed with 150  $\mu$ L DI water, 120  $\mu$ L IPA solution, and 30  $\mu$ L Nafion solution. The mixture was sonicated at 37 kHz and 100 W. After sonication, 2.5  $\mu$ L of catalyst ink was applied to the cleaned GCE and left overnight before employing as working electrode. Figure 1 shows a schematic diagram for the setup of CV and CA analysis.

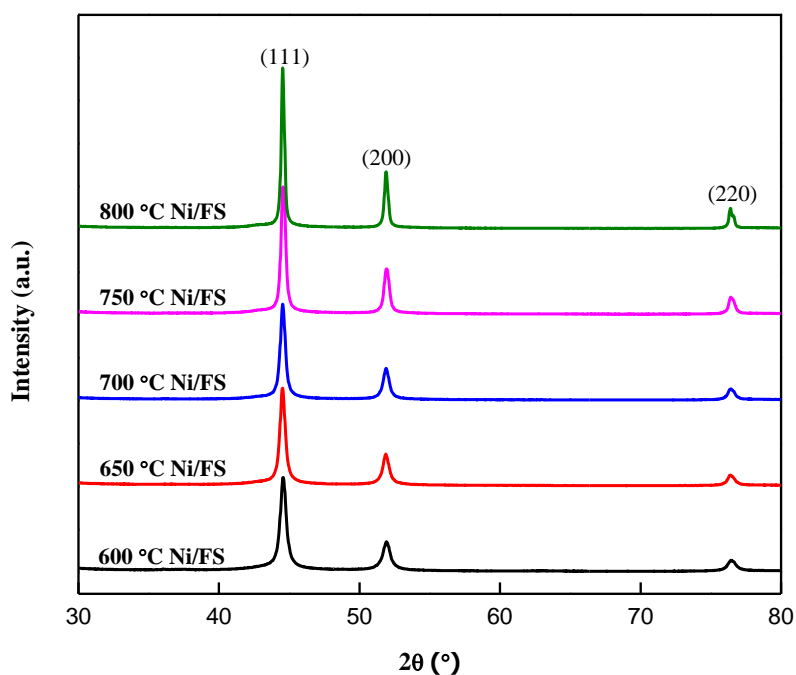


**Fig. 1.** Schematic diagram for the setup of CV and CA analysis (a) counter electrode, (b) reference electrode, (c) working electrode

## 3. Results and Discussion

### 3.1 Phase and Crystallinity of Ni/FS Electrocatalyst

The X-ray diffraction (XRD) patterns were utilized to validate the crystallographic structure and surface chemical composition of Ni/FS at various calcination temperatures (Figure 2). Based on the X-ray diffraction (XRD) pattern obtained for all synthesized Ni/FS samples, it can be deduced that the presence of a metallic nickel phase has been seen. Strong diffraction peaks were seen at 2 $\theta$  of 44.66°, 51.83°, and 76.43°, which can be attributed to the crystal diffraction planes (1 1 1), (2 0 0), and (2 2 0), respectively, of pure nickel as indicated by the ICDD reference card with the code 00-001-1258 (Sayed *et al.*, 2023). The intensities of all diffraction peaks exhibited a notable increase with an elevation in calcination temperature, suggesting a pronounced improvement in the crystallization of the nickel phase.

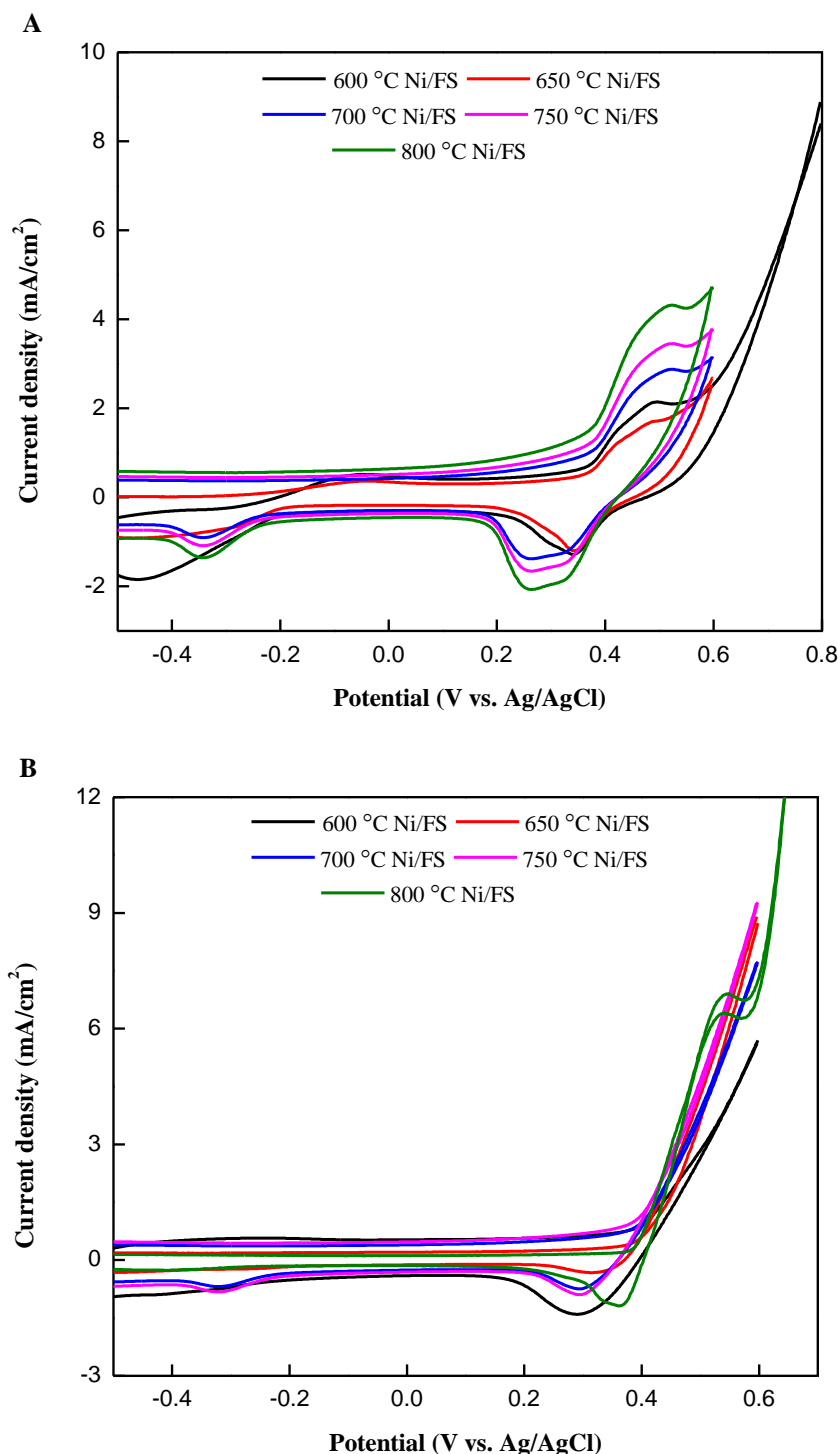


**Fig. 2.** XRD patterns of different calcination temperature of 600 °C, 650 °C, 700 °C, 750 °C, and 800 °C

### 3.2 Catalytic Activity of Ni/FS Electrocatalyst

Figure 3A shows the cyclic voltammograms of Ni/FS in the 1 M NaOH solution. According to the electrochemical behavior of nickel electrode in alkaline electrolyte, thin layer of Ni(OH)<sub>2</sub> forms spontaneously on nickel surface and nickel is electrochemically passivated by Ni(OH)<sub>2</sub> coating [13]. As can be seen in Figure 3A, peak in the anodic direction at 0.52 V was observed on CV of all sample, which represents the oxidation of Ni(OH)<sub>2</sub> to the nickel oxy-hydroxide (NiOOH). Meanwhile, the peak could be observed in the cathodic direction at 0.34 V. This peak can attribute to the reduction of NiOOH to Ni(OH)<sub>2</sub> [10], in accordance with the following reaction as in Eq. (1).





**Fig. 3.** Cyclic Voltammograms for Ni/FS in (a) 600 °C, (b) 650°C, (c) 700 °C, (d) 750 °C, and (e) 800 °C of (A) 1.0 M of NaOH and (B) 1.0 M of NaOH +1.0 M EtOH with constant rate of 10 mV/s

The calcination temperature has an impact on the crystal formation, which subsequently influences the electrocatalytic activity. The electrocatalytic activity is seen to increase linearly with increasing calcination temperature (Figure 3B). The Ni/FS synthesized at a temperature of 800 °C demonstrated superior performance compared to others temperature. The obtained results indicate that the oxidation peak values were recorded as 2.10, 2.50, 2.60, 6.50, and 6.93 mA/cm<sup>2</sup> at calcination

temperature of 600 °C, 650 °C, 700 °C, 750 °C, and 800 °C, respectively, listed in Table 1. Therefore, it can be suggested that elevating the calcination temperature results in enhanced electric conductivity, thereby facilitating electron transport [5,14]. This is evident from the observed increase in current density. The evaluation of tolerance to accumulated intermediates, namely CO, critically depends on the ratio of the forward scan peak current ( $I_F$ ) to the backward scan peak current ( $I_B$ ), denoted as  $I_F/I_B$ . In general, catalysts that have a greater  $I_F/I_B$  ratio tend to demonstrate enhanced performance in the oxidation of ethanol to  $CO_2$ . From Table 1, at 800 °C, Ni/FS has the highest  $I_F/I_B$  ratio, which means that more intermediate carbonaceous chemicals are being turned into  $CO_2$ .

**Table 1.**  $I_F/I_B$  ratio for various calcination temperature of Ni/FS

Electrocatalyst	Oxidation peak current, $I_F$ (mA/cm <sup>2</sup> )	Reduction peak current, $I_B$ (mA/cm <sup>2</sup> )	$I_F/I_B$ ratio
600 °C Ni/FS	2.10	2.03	1.03
650 °C Ni/FS	2.50	2.38	1.05
700 °C Ni/FS	2.60	2.49	1.04
750 °C Ni/FS	6.50	6.01	1.07
800 °C Ni/FS	6.93	6.31	1.10

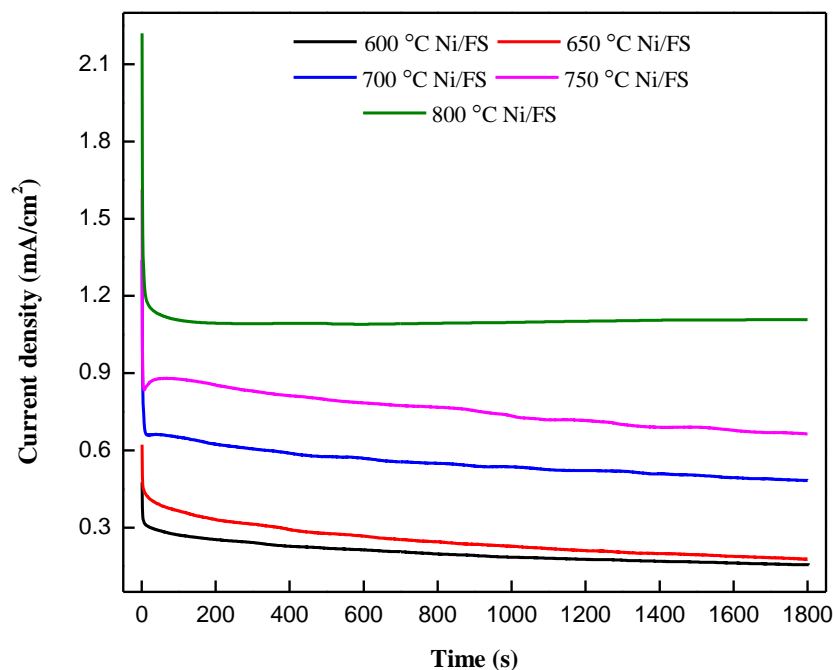
### 3.3 Stability of the Ni/FS Electrocatalyst

The analysis results of CA curves for 600 °C, 650 °C, 700 °C, 750 °C, 800 °C of Ni/FS achieved at room temperature using 1.0 M NaOH + 1.0 M EtOH solution at a constant potential of 0.4 V for 1800 s as shown in Figure 4. Retention rate is used to determine the stability of the electrocatalyst and to determine whether it is electrochemically active. Eq. (2) was used to calculate the retention rate for all the samples. From Table 2, it can be observed that 800 °C Ni/FS has the highest retention rate compared with the other samples with different calcination temperature. This shows that 800 °C Ni/FS has the best stability and electrochemical activity.

$$\text{Retention rate (\%)} = \frac{I_{\text{final}}}{I_{\text{initial}}} \times 100\% \quad (2)$$

**Table 2.** Retention rates ratio for all Ni/FS samples

Sample	$I_{\text{initial}}$	$I_{\text{final}}$	Retention rate (%)
600 °C Ni/FS	0.48	0.15	31.25
650 °C Ni/FS	0.62	0.18	29.03
700 °C Ni/FS	1.34	0.48	35.82
750 °C Ni/FS	1.61	0.66	40.99
800 °C Ni/FS	2.22	1.11	50.00



**Fig. 4.** Chronoamperometry for Ni/FS in 1.0 M of NaOH+1.0 M EtOH at a constant potential of 0.4 V for 1800 s (a) 600 °C, (b) 650 °C, (c) 700 °C, (d) 750 °C, (e) 800 °C

#### 4. Conclusions

The wet impregnation approach was employed for successfully producing Ni/FS catalysts in this study. The objective to analyze the electrochemical properties of different calcination temperature of nickel supported on candle soot towards EOR was achieved. The XRD analysis reveals that the Ni/FS catalysts exhibit a significant degree of crystallinity in the metallic nickel phase. The electrochemical properties were analyzed by using two methods, which were CV and CA. CV analysis examined the electrochemical characteristics of Ni/FS with the calcination temperature of 600, 650, 700, 750, and 800 °C. From the analysis, it was concluded that 800 °C exhibits the highest current density (6.93 mA/cm<sup>2</sup>). The observed increase in current density is attributed to the enhancement in electric conductivity resulting from the elevation of calcination temperature. This, in turn, facilitates electron transport. Apart from that, CA analysis proved that 800 °C Ni/FS has the best stability of electrocatalyst and electrochemically active when candle soot was used as catalyst support by obtaining the highest retention rate (50.00 %). The improved catalytic activity and enhanced stability observed in the Ni/FS electrocatalyst can be attributed to the synergistic interaction between nickel (Ni) and the carbonaceous material derived from candle soot.

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