



## Material characterization and electrochemical performance of copper-based rare earth composite oxide electrodes for use in ammonia electrocatalytic oxidation

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### ABSTRACT

The process of electrochemical oxidation (ECO) of ammonia (NH<sub>3</sub>) is becoming an increasingly important issue in environmental electrochemistry and has various prospective applications. A copper-based rare earth electrode material was synthesized by coprecipitation of a mixture that included copper, lanthanum, and cerium nitrate salts, and this material was applied in a typical electrocatalytic reaction, such as NH<sub>3</sub>-ECO, for fuel cell applications. In this study, the ability to oxidize ammonium for ECO while immersed in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution was evaluated using a cyclic voltammetry (CV) technique. The changes in the properties of the electrocatalytic materials were analyzed using UV-vis absorption spectra, fluorescence spectroscopy (FS), and environmental scanning electron microscopy, revealing that the activity of the copper-based rare earth electrode materials utilized a high potential scan rate. The maximum current density was reached when the NH<sub>3</sub>-ECO voltage was -0.1 V. The reversible redox ability during CV may explain the high activity of the catalysts, suggesting the presence of a synergetic effect between the copper-based composite materials. Additionally, the FS displayed three fluorescence peaks with excitation wavelengths of 265, 450, and 500 nm at room temperature before the reaction. These excitation peaks can be attributed to a metal-enhanced fluorescence effect that is associated with the copper clusters on the electrocatalyst surface during the reaction, proving that FS is an appropriate and effective tool for characterizing the copper clusters that enhance the intrinsic fluorescence characteristics of Cu-La-Ce composite within catalytic treatment systems. When observing the UV-vis absorption spectra for the copper (II) species, the peak absorbance value was at 220 nm.

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## 1. Introduction

Ammonia (NH<sub>3</sub>) is a serious nitrogen-containing contaminant that attracts widespread concerns because it is an environmental obstacle that contributes to the acidification and eutrophication of natural resources day by day. The electrocatalytic oxidation of NH<sub>3</sub> has been proposed as a new technology that removes undesirable nitrogen compounds for environmental purpose, such as nitrate ions, that are discharged into the environment and it is an economical process for generating high-purity H<sub>2</sub> for fuel cells rather than producing methanol [1].

In addition to being environmentally friendly methodology, the electrocatalytic oxidation of ammonia (NH<sub>3</sub>-ECO) to form H<sub>2</sub> and N<sub>2</sub> reduces NH<sub>3</sub> pollution and may be applied to direct ammonia fuel cells [2]. Additionally, NH<sub>3</sub> is a clean H<sub>2</sub> energy carrier that has a potential application in fuel cells, providing an additional bonus regarding environmental protection [3]. These benefits explain why researchers in materials chemistry have recently begun to develop heterogeneous catalytic process. In the past, the oxidation process has been improved using high-performance catalysts that potentially shorten the reaction time and promote a complete reaction under mild operating conditions [4,5]. It is well known that the electrochemical oxidation (ECO) of NH<sub>3</sub> has been studied in detail in an alkaline solution with platinumized platinum; the lone pair electrons on NH<sub>3</sub> in its basic form render it more vulnerable to oxidation than NH<sub>4</sub><sup>+</sup> [6]. Most electrochemical studies regarding NH<sub>3</sub> oxidation have utilized platinum as an electrode material. Unfortunately, some reaction intermediates and adsorbed species deactivate the platinum during NH<sub>3</sub>-ECO. However, N<sub>ads</sub> poisons the platinum surface because the adsorption energy of N<sub>ads</sub> on platinum is too high for the two N atoms to recombine, thereby precluding nitrogen formation. The literature indicates that the vast majority of NH<sub>3</sub> electrocatalytic reactions are structurally sensitive, while the crystallographic surface orientation profoundly affects the stability, selectivity, and activity of these processes [7]. Liu et al. [8] reported that the electrocatalytic activity of a Pt electrocatalyst prepared via electrodeposition on an ITO substrate for NH<sub>3</sub> oxidation in aqueous solutions strongly depended on the surface morphology of the Pt particles. Vitse et al. [9] selectively converted NH<sub>3</sub> in alkaline electrolytic cell to produce H<sub>2</sub>

with high purity while using an electrodeposition Pt–Ir bimetallic catalyst during electrolytic processes. Yao and Cheng [10] developed a binary Ni–Pt alloy electrode for electrocatalytically oxidizing NH<sub>3</sub>, proving that the fresh Ni–Pt catalyst became more active as the temperature increased during NH<sub>3</sub> decomposition; however, the rate-limiting step for NH<sub>3</sub> diffusion toward the electrode surface is critical during the NH<sub>3</sub> electro-oxidation process. Liu et al. [11] investigated NH<sub>3</sub> decomposition to produce CO<sub>x</sub>-free H<sub>2</sub> in a fixed-bed continuous-flow quartz reactor at 873 K when GHSV = 46,000/h, demonstrating that the NH<sub>3</sub> conversion reached 96% over a Ni/SBA-15 catalyst. Hung [12] examined the selective catalytic oxidation of NH<sub>3</sub> in a gaseous stream with a nanoscale platinum-based ternary catalyst with a 6:4 molar ratio at 423–673 K while GHSV = 92,000/h. A synergistic effect occurred with a trimetallic nanoscale structure that generated the strongest NH<sub>3</sub> reduction activity due to its high catalytic ability and excellent chemical stability. Moreover, copper, lanthanum, and cerium metals with fluorite-type oxides are synergistic when they are prepared as a composite Cu–La–Ce catalyst [13]. Vot et al. [14] investigated an innovative pulse method for electrodepositing Pt on a glassy carbon substrate while generating the largest amount of Pt (100) terraces to achieve the highest electrocatalytic activity for NH<sub>3</sub> oxidation. However, Pt electrodes deactivate over time during NH<sub>3</sub>-ECO because adsorbed N-species generated from oxidized NH<sub>3</sub> poison the electrode.

Electrochemical cyclic voltammograms have been conducted in most works to evaluate the electrochemical activity of each catalyst. Moreover, according to our previous research [15], fluorescence spectroscopy (FS) data may be used to compare the variations in the properties of the catalysts before and after the reaction. Studies of fluorescence emissions, especially of the copper-based polymetallic materials, which have been used for decades, are available, but there is little information about the fluorescence of most of the newly developed materials and their interactions with metal structures. Herein, FS spectroscopy was used as an effective way to provide available information to understand the catalyst characteristics during the electrocatalytic process. To facilitate the application of the electrocatalytic oxidation technique, the activity of Cu–La–Ce electrocatalysts during NH<sub>3</sub> oxidation in an acidic medium under varying reaction parameters was

investigated using CV processes, and a surface analysis was conducted using spectrometric techniques including UV–vis, FS, and environmental scanning electron microscopy (ESEM).

## 2. Materials and methods

### 2.1. Preparation of the composite catalysts

The copper-based rare earth composite catalysts used in this study were prepared via co-precipitation of copper (II) nitrate (GR grade, Merck, Darmstadt, Germany), lanthanum (II) nitrate (GR grade, Merck, Darmstadt, Germany), and cerium (III) nitrate in a 6:2:2 molar ratio in a similar way to that previously reported [5,13]. The precipitate was washed with distilled water before being dried at 473 K for 10 h. Subsequently, the catalysts were calcined at 773 K in flowing air for 4 h. The powder was processed into tablets using 0.1 N acetic acid as a binder. The tablets were sequentially reheated at 573 K to burn off the binder and then crushed. Finally, particle sizes from 0.15 to 0.25 mm were obtained using screens with different mesh sizes.

### 2.2. Experimental procedure

The Cyclic voltammograms were measured at room temperature with an electrochemical analyzer (CHI 6081D, USA) equipped with three-electrode electrochemical cells to investigate the electrochemical behaviors of the electrode samples. A glassy carbon electrode (3 mm in diameter, CHI 104, USA) loaded with active Cu–La–Ce samples was used as the working electrode and scanned at 5, 10, 50, and 100 mV/s while the potential cycled between  $-0.2$  and  $1.2$  V. The platinum wire (CHI 102, USA) and standard hydrogen electrode were used as the counter electrode and the reference electrode, respectively. The electrolyte solution was 0.5 M of  $\text{H}_2\text{SO}_4$ . Before the CV measurements, the electrolyte solution was degassed via bubbling with nitrogen. The UV–vis absorption spectra (U-2900, Hitachi, Japan) and fluorescence spectrophotometer (F-4500, Hitachi, Japan), respectively, were used to examine the surface properties of a suspended colloid prepared from solid samples in distilled water. Regarding fluorescence spectrophotometer, it pairs the excitation spectra on the  $x$ -axis and emission spectra on the  $y$ -axis corresponded to the fluorescence intensity. The widths of both slits at the excitation and emission monochromators were 10 nm. During this investigation, the fluorescence spectra comprised 60 excitation and 60 emission spectra from 200 to 800 nm to yield discrete values of fluorescence intensity at

3600 excitation/emission wavelength pairs. Spectral subtraction was performed to remove the blank spectra generated from pure water. ESEM (Quanta 200 FEG, FEI Company, Czech Republic) revealed the catalyst morphology and structure of the Cu–La–Ce composite on the catalyst surface.

## 3. Results and discussion

The CV curves at different scan rates (5–100 mV/s) in a 0.5 M  $\text{H}_2\text{SO}_4$  medium are plotted in Fig. 1. The Cu–La–Ce electrocatalyst displayed little reactivity in the potential window when the scan rates were 5 and 10 mV/s. Notably, the CV curves revealed that the

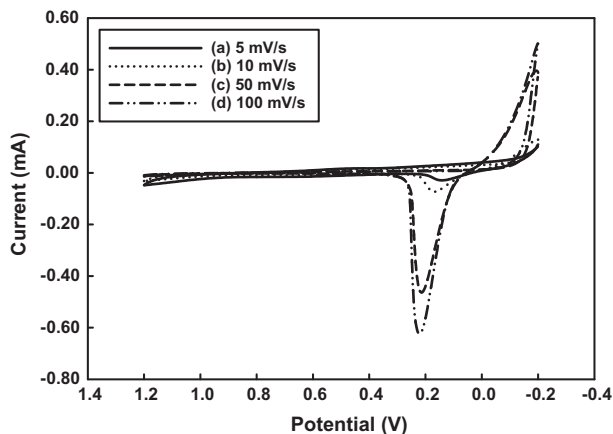


Fig. 1. Cyclic voltammogram profiles in a 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte solution recorded at various scan rates for the Cu–La–Ce electrocatalyst.

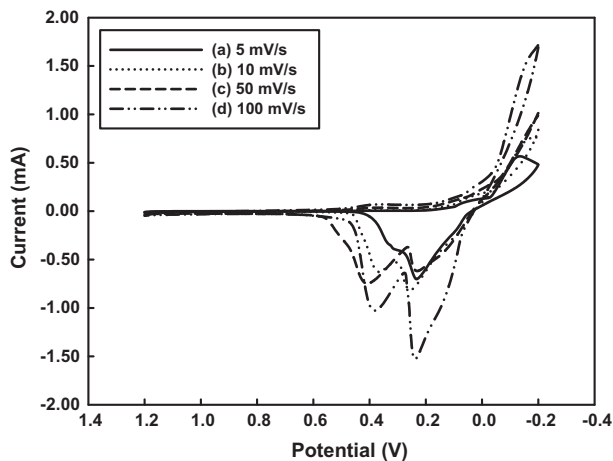


Fig. 2. Cyclic voltammogram profiles in a 0.5 M  $\text{H}_2\text{SO}_4$  + 0.1 M  $\text{NH}_3$  solution electrocatalytically recorded at various scan rates for the Cu–La–Ce electrocatalyst.

Cu–La–Ce electrocatalyst displayed superior reduction capacities because well-marked oxidation peaks appeared at 0.2 and  $-0.1$  V and increased its respective current density under higher potential scan rates (50 and 100 mV/s). The increased current density that occurred when increasing the potential scan rate may be attributed to the charged interface capacitance caused by the charge transfer process [9]. In a cyclic voltammetric investigation, the peak current density for this type of electrochemical reaction was approximately 0.2 V because the reaction involved a strong hydrogen adsorption [16]. Additionally, Vot et al. [14] investigated  $\text{NH}_3$  ECO in 0.5 M  $\text{H}_2\text{SO}_4$ , characterizing the hydrogen adsorption/desorption (between  $-0.2$  and 0.2 V) and the double layer (between 0.2 and

0.6 V) regions using CV. Compared to our findings, the electrochemical behavior of the catalyst is related to both the  $\text{NH}_3$  oxidation and the surface composition of catalyst.

Investigation of the properties of the Cu–La–Ce electrocatalyst is a crucial part of this research. Fig. 2 displays the CV profiles at scan rates from 5 to 100 mV/s while 0.1 M  $\text{NH}_3$  was added to a 0.5 M  $\text{H}_2\text{SO}_4$  medium for the oxidation reaction. Fig. 2 reveals that a rapid increase trend in the oxidation current density did not appear until approximately 0.5 V when scanning at 10, 50, and 100 mV/s, respectively, because the adsorption of the  $\text{NH}_3$  at the electrode surface hindered the hydroxyl ion or oxide layer formation on the catalyst, changing the electrode–electrolyte interfacial

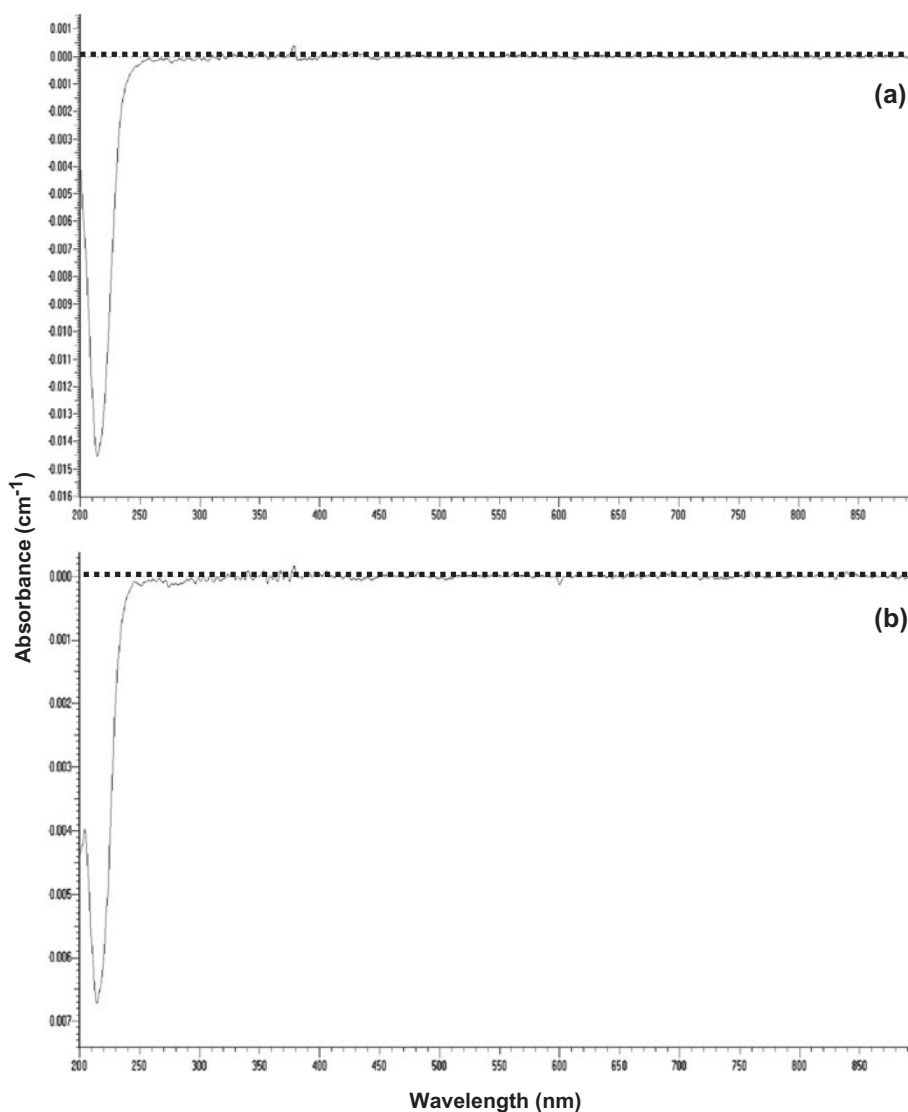


Fig. 3. UV–vis absorption spectra of the Cu–La–Ce electrocatalyst taken (a) before and (b) after the CV tests.

properties in the solution. Based on the literature data,  $\text{NH}_3$  initiates its oxidation at 0.45 V in the double-layer region of platinum and reaches its maximum activity at approximately 0.6 V [17]. Furthermore, the CV plots reveal that the Cu–La–Ce electrocatalyst had a wide peak current density at approximately 0.25, 0.4, and  $-0.1$  V. This reactivity pattern may indicate that not enough electrochemical surface active catalytic sites necessary for dehydrogenation the ammonia oxidation were formed [18]. After passing this peak, the decrease in current density may be affected by the formation of adsorbed nitrogen atoms ( $\text{N}_{\text{ads}}$ ) [19]. Additionally, Gerischer and Mauerer [20] proposed that  $\text{N}_2$  is formed at positive potentials with quantitative current via dimerization of dehydrogenated  $\text{NHx}_{(\text{ads})}$ . Moreover, the  $\text{NH}_3$  and  $\text{O}_2$  adsorbed onto specific sites on the Cu–La–Ce electrocatalyst might promote the rapid conversion from  $\text{NH}_3$  to  $\text{H}_2$  and  $\text{H}_2\text{O}$ , thus minimizing the formation of harmful nitrogen oxides. Furthermore, the catalytic activity may have been strengthened by the robust interaction among the composite copper, lanthanum, and cerium. Interestingly, the Cu–La–Ce electrocatalytic materials scanned at 5 and 10 mV/s exhibited a decrease in the  $\text{NH}_3$  oxidation peak currents in the given potential window (Fig. 2).

To identify the chemical properties of the Cu–La–Ce catalyst, Fig. 3 presents the UV–vis absorption spectra describing on the states of the metallic species in the catalysts. As displayed in Fig. 3(a), the peak location associated with a copper (II) species before the reaction with  $\text{NH}_3$  was observed at 220 nm, and the UV–vis absorption spectra displayed only minor changes after the activity test (Fig. 3(b)). The EEFMs of the Cu–La–Ce catalyst before and after the activity test are shown in Fig. 4. Fig. 4(a) reveals that the fluorescence spectra for the fresh Cu–La–Ce electrocatalyst had three significant excitation peaks at 265, 450, and 500 nm. These

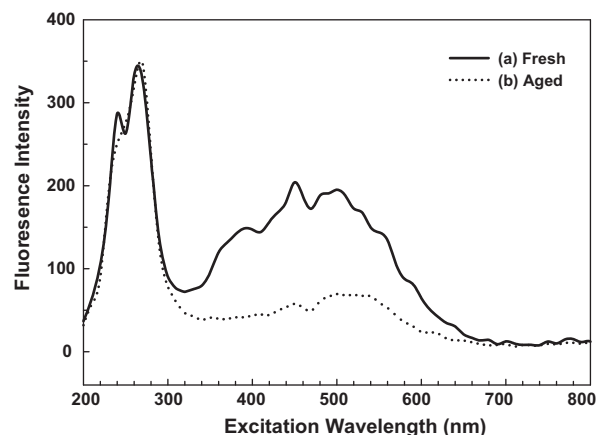


Fig. 4. The fluorescence spectra of the Cu–La–Ce electrocatalyst taken (a) before and (b) after the CV tests.

excitation peaks exhibited a metal-enhanced fluorescence effect caused by the copper clusters on the Cu–La–Ce electrocatalyst surface during the reaction. A similar report appeared in the research of Cano-Raya et al. [21], proving that the fluorescence excitation wavelengths of copper were, respectively, at 265–340 nm and 465–510 nm. However, an obvious divergence in the fluorescence spectra of Cu–La–Ce electrocatalyst after activity test is revealed in Fig. 4(b). Additionally, the fluorescence intensity decreased with increasing excitation wavelengths. These changes in fluorescence spectra for the catalyst may be related to the lowered availability of the electroactive sites on the electrodes and the over oxidation of the Cu–La–Ce electrocatalyst surface active sites during the reaction.

Fig. 5 presents the changes in the surface morphology and structure of the Cu–La–Ce composite catalyst, as elucidated by ESEM. These data provide important

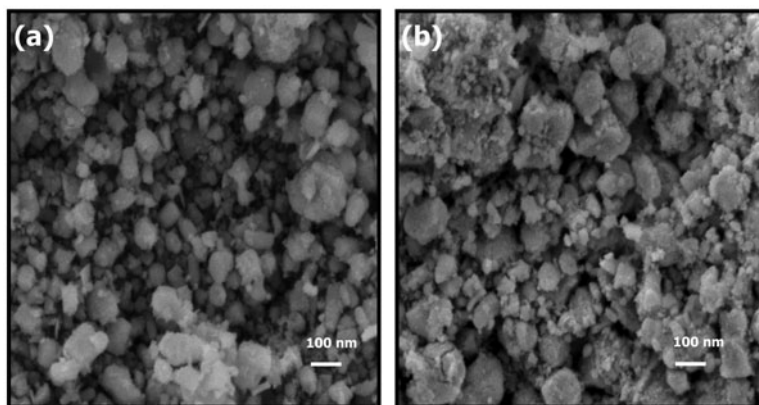


Fig. 5. ESEM photographs of the (a) fresh and (b) exhausted Cu–La–Ce electrocatalyst.

information regarding the structure of the catalyst surface during  $\text{NH}_3$  oxidation. The agglomerates observed by ESEM indicate that the composite catalyst particles form fine grains and prickly sphere-like species (Fig. 5(a)). However, Fig. 5(a) also reveals that the catalyst surface is more monodispersed and well crystallized than the surface shown in Fig. 5(b). These small crystalline phases may explain that the high catalytic activity is due to the highly dispersed nanoscale particles (~100 nm). Specifically, disaggregated phases formed as the catalyst surface aged or was poisoned via plugging, implying that the porosity of the particles had changed (Fig. 5(b)). Moreover, this change in porosity might also explain the increased over-potential of the catalytic reaction, and therefore the decline in the performance of the  $\text{NH}_3$  oxidation. As a result, the electrocatalytic activity of the prepared Cu–La–Ce composite catalyst for the  $\text{NH}_3$  oxidation in aqueous solutions depends on the surface crystalline phases of composite particles.

#### 4. Conclusions

In summary, the surface peak current density and potential electrochemical characterizations of Cu–La–Ce electrocatalytic materials led to a significant enhancement in the catalytic performance during ECO- $\text{NH}_3$  reaction using a CV technique. The wide current density peak for the  $\text{NH}_3$  oxidation proves that catalyst displays excellent activity across a wide potential range. Notably, the Cu–La–Ce electrocatalyst underwent further reduction with higher potential scan rates. Consequently, the Cu–La–Ce electrocatalyst is critical during the  $\text{NH}_3$  electrocatalytic process. Moreover, UV–vis absorption spectra for the copper (II) species with the peak absorbance value were at 220 nm. According to a fluorescent spectrometry evaluation, Cu–La–Ce electrocatalyst yielded fluorescent peaks at 265, 450, and 500 nm at room temperature. Consequently, an electrochemical performance and material characterization revealed that the electro-oxidation ability may explain the significant activity of the catalysts based on the CV over a wide potential range.

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