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Electro-Oxidation of Ammonia over Copper Oxide Impregnated γ -Al₂O₃ Nanocatalysts

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Abstract: Ammonia electro-oxidation (AEO) is a zero carbon-emitting sustainable means for the generation of hydrogen fuel, but its commercialization is deterred due to sluggish reaction kinetics and the poisoning of expensive metal electrocatalysts. With this perspective, CuO impregnated γ -Al₂O₃ (CuO/ γ -Al₂O₃) hybrid materials were synthesized as effective and affordable electrocatalysts and investigated for AEO in alkaline media. Structural investigations were performed via different characterization techniques, i.e., X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electrochemical impedance spectroscopy (EIS). The morphology of γ -Al₂O₃ support as interconnected porous structures rendered the CuO/ γ -Al₂O₃ nanocatalysts with robust activity. The additional CuO impregnation resulted in the enhanced electrochemical active surface area (ECSAs) and diffusion coefficient and spiked the electrocatalytic performance for NH₃ electrolysis. Owing to good values of diffusion coefficient for AEO, low bandgap, and availability of ample ECSA at higher CuO to γ -Al₂O₃ ratio, these proposed electrocatalysts were proved to be effective in AEO. Due to good reproducibility, electrochemical stability, and higher activity for ammonia electro-oxidation, CuO/ γ -Al₂O₃ nanomaterials are proposed as efficient promoters, electrode materials, or catalysts in ammonia electrocatalysis.

Keywords: CuO/ γ -Al₂O₃; ammonia electro-oxidation (AEO); electrochemical surface area (ECSA); electrocatalysts

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1. Introduction

Ammonia (NH₃) is a corrosive, pungent and carcinogenic inorganic gaseous pollutant and is being produced from both biogenic and anthropogenic sources, i.e., livestock waste, animal agriculture, refrigeration, nitrogen fertilizer and petroleum refining industries [1,2]. Many efforts have been devoted to removing NH₃ from gaseous and waste streams through chemical, biological, and physical methods, but all have their limitations [2–4]. Recently, electrocatalytic oxidation of ammonia (AEO) has attracted much attention of researchers and scientists because, as a hydrogen-rich carrier, it possesses 70% higher volumetric hydrogen content than pure liquid hydrogen [5,6]. Theoretical and experimental investigations reveal that hydrogen generation via ammonia electro-oxidation (AEO) is a cost-effective approach compared to water electrolysis because it requires much lower oxidation potential (0.06 V) than water (−1.23 V), as described in Equations (1–3) [7,8]. Theoretical ammonia electrolysis consumes energy of about ~1.55 Wh·g^{−1} H₂ at standard conditions, which is 95% less than water electrolysis [9]. Due to fast reaction kinetics and modest operating conditions, ammonia electro-oxidation is considered a promising future technology to

produce hydrogen from ammonia polluted wastewaters [10,11]. At 25 °C, the ammonia electrooxidation potential is -0.77 V vs. Standard Hydrogen Electrode (SHE), merely 0.06 V less negative than the oxidation potential of -0.83 V vs. SHE for hydrogen evolution in alkaline solution [12].

Electro-oxidation of ammonia prompts the inhibition of the oxygen evolution reaction (OER) because of adsorption of the products in result of ammonia oxidation on the electrode surface. The OER inhibition boosts the AEO reaction, which is the main reaction. The amino radicals as intermediates, formed in the course of ammonia oxidation, trigger a reaction chain where dissolved molecular oxygen is involved in the AEO [13]. Nitrogen present as ammonia or ionized ammonium or both forms deplete dissolved oxygen through oxidation in aqueous solutions, which boost the AEO reaction [14].

Moreover, innovation in the design and fabrication of reasonable and proficient electrocatalysts for AEO are essential for its successful implementation. To commercialize this direct ammonia fuel cell (DAFC) technology, an efficient, stable, and economical electrocatalyst is required. Thus far, expensive noble metal-based (Pt, Ru, Ir, Rh, Pd) alloys are considered as the best performing AEO catalysts [5–8,15,16]. Sluggish reaction kinetics of AEO, high cost and low resistance to poisoning by reaction intermediates of these catalysts hinder this technology in commercialization. Recently, some effort has been devoted to developing non-noble metal electrocatalysts including NiO-TiO₂ [17] and CuO-TiO₂ [1] for AEO, but they require higher overpotential. Similarly, Ni oxides and hydroxides-based catalysts have displayed better performance towards AEO; however, they get easily corroded and deactivated in ammonia solution [9,17,18]. Although it is proved theoretically that copper displays comparable activity to Pt, it forms too weak a bond with Ni than Pt, leading to a very high overpotential [19]. Therefore, it displays poor catalytic performance toward AOR experimentally [20]. Cupric oxide (CuO) is a promising p-type semiconductor and has been investigated in various applications such as photocatalytic hydrogen production [21], dye degradation [22], electro-oxidation of hydrazine [23–25], methanol oxidation [26], and so on. Recently, the oxidation behavior of CuO-modified TiO₂ was investigated for ammonia ($0.5 \text{ M H}_2\text{SO}_4 + 0.1 \text{ M NH}_3$) by using linear sweep voltammetry [1]. However, extensive research is required to explore the cost-effective and efficient electrocatalysts to replace the incumbent Pt-based alloys [27]. Porous materials behave as potential electrodes owing to their high conductivity [28].

Furthermore, catalyst support materials exhibit great influence on the cost, performance, and durability of polymer electrolyte membrane (PEM) fuel cells. Due to high chemical/electrochemical stability, surface area and versatility, the high surface area metal oxides including alumina ($\gamma\text{-Al}_2\text{O}_3$), silica (SiO₂), titania (TiO₂) and zirconia (ZrO₂) are considered as better catalyst supports than conventional carbon materials [29–32]. Besides, multiple types of transition alumina are recurrently used as supports for developing heterogeneous catalysts which consist of an active phase dispersed on a carrier or support. Alpha (α), beta (β) and gamma (γ) are three different types of alumina. The $\alpha\text{-Al}_2\text{O}_3$, also known as nano-alumina, is a white puffy powder. It has lower specific surface area, limited high temperature resistance and it is inert, therefore it does not belong to activated alumina, and hence displays almost no catalytic activity. $\beta\text{-Al}_2\text{O}_3$ is hexagonal, with lamellar structure and the unit cell contains two alumina spinel-based block. It also exhibits low catalytic and strengthening properties. Among the different known alumina types, $\gamma\text{-Al}_2\text{O}_3$ is perhaps the most important with direct application as a catalyst support in the several industries. $\gamma\text{-Al}_2\text{O}_3$ possesses high purity and provides excellent dispersion and high specific surface area, offering commendable resistance to high temperature and high activity. It is porous; hence, it is said to be activated alumina and used as catalyst

support as well as adsorbent [33]. The efficacy of γ - Al_2O_3 can be regarded to an auspicious combination of its textural possessions, e.g., surface area, pore volume, pore-size distribution and acid/base characteristics, which are mainly related to local microstructure, surface chemical composition and phase composition [34]. The highly porous γ - Al_2O_3 can be synthesized at moderate temperatures; therefore, it is widely used as support in many applications [22,26,35,36].

Herein, cost-effective and easily synthesized electrocatalysts ($\text{CuO}/\gamma\text{-Al}_2\text{O}_3$) were investigated for efficient ammonia electro-oxidation reaction in alkaline media. The CuO impregnated $\gamma\text{-Al}_2\text{O}_3$ nanomaterials were prepared by a simple impregnation-annealing process [26]. In such systems, impregnation of $\gamma\text{-Al}_2\text{O}_3$ with an aqueous active metal salt, preceded by drying and calcination, typically results in diffusion of active metal ions into the support surface, forming interaction species. Depending on the calcination temperature and time, only a finite amount of metal ions can be accommodated in the vacant lattice sites of the support. Once all of the available lattice sites are saturated, further addition of metal ions can be accommodated only by segregation of a separate metal oxide phase. The morphology of $\gamma\text{-Al}_2\text{O}_3$ support was modulated from plate-type to network-like by altering the CuO contents in compositions [37]. The electrocatalytic performance of as-synthesized $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ was observed by using cyclic voltammetry as the investigation tool. The prepared nanomaterials displayed high electrochemical active surface areas (ECSA), diffusion coefficients, and electrocatalytic activity for NH_3 electro-oxidation. Also, the conductive and stable catalytic performance towards ammonia electro-oxidation is indebted to their low bandgaps. Increasing the CuO contents in $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ nanomaterials enhanced the catalytic performance because of the suppressed formation of active reaction intermediates as observed via CV profiles. The electrochemical stability and higher performance towards the ammonia electro-oxidation rendered the $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ nanomaterials as efficient electrocatalysts.

2. Experimental

2.1. Preparation of $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ Electrocatalysts

All chemicals were purchased from Sigma Aldrich, St. Louis, MO, USA. and were used without further purification. Firstly, the catalyst's support alumina ($\gamma\text{-Al}_2\text{O}_3$) was prepared by calcination of pre-precipitated aluminum hydroxide ($\text{Al}(\text{OH})_3$). Typically, 36.2 g of aluminum nitrate nonahydrate ($\text{Al}_2(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was dissolved in distilled water (50 mL) and aqueous ammonia (35%) was added dropwise to obtain the white precipitates of aluminum hydroxide. Finally, as-prepared vacuum dried (80 °C) powder was calcined in NEY 2-525 furnace at 800 °C in the air for two hours to obtain $\gamma\text{-Al}_2\text{O}_3$. The copper oxide coated alumina ($\text{CuO}/\gamma\text{-Al}_2\text{O}_3$) nanomaterials were synthesized in two-steps; in the first step, as-synthesized $\gamma\text{-Al}_2\text{O}_3$ was impregnated in the required amount of aqueous solution of copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) for 48 h. and dried in an oven at 200 °C. The X- $\text{CuO}/\text{Al}_2\text{O}_3$ (X = 4, 8, 12, 16 and 20 wt.% of CuO) impregnated catalysts were obtained by calcination at 500 °C in the air for two hours as shown in Figure 1. The gradual variation in color of synthesized catalysts from bluish-white to bluish green was observed with incremental CuO content.

2.2. Electrochemical Investigations

Electrochemical analysis of all prepared electrocatalysts was carried out by using Gamry potentiostat interface 1000 and three-electrode system in which silver/silver chloride (Ag/AgCl), silver wire and modified glass carbon electrode are used as a reference, counter and the working electrode, respectively [38–40]. Ag/AgCl does not interfere with the system under investigation as it has been used as a reference electrode in ammonia and other basic media [41–43]. Silver wire is also used as a conductive counter electrode without affecting the system performance [44]. The glassy carbon electrode was polished with alumina slurry and cleaned with ethanol before dropping the catalyst ink that was prepared in ethanol while 5% Nafion (2.0 μL) solution was poured on the powder catalyst

as a binder. The electrochemical active surface areas (ECSAs) of all electrocatalysts were determined in a standard redox solution (5.0 mM $K_4[Fe(CN)_6]$ + 3.0 M KCl) at a scan rate of 100 mVs^{-1} . Ammonia electro-oxidation was conducted by cyclic voltammetry (CV) in 1.0 M solution of NH_3 prepared in 0.1 M KOH solution.

Figure 1. Graphical abstract for the synthesis of $CuO/\gamma-Al_2O_3$ nanomaterials for ammonia electro-oxidation.

3. Results and Discussion

3.1. Structural Characterization

The phase purity and crystal structure of all prepared samples was determined by powder X-ray diffraction (PXRD) with a scan rate 0.4° per minute in 2θ window of 10° – 70° via continuous scan type using PANalytical X'PERT High Score's diffractometer, Malvern, UK. As shown in Figure 2a, the diffraction peaks at 32.4° and 36.7° are assigned to CuO which become more prominent as the loading of CuO is increased from 4% to 20%, while 37° , 61.5° and 68.1° corresponds to Al_2O_3 . All these peaks have been indexed for pure cubic system and corresponded to JCPDS card No. 45-0937 [26]. There is no visible diffraction peak shift due to addition of Cu contents which indicates CuO species on the alumina surface exist as highly dispersed species [45]. Moreover, if 20%-CuO/ Al_2O_3 is compared with pure alumina and 4%-CuO/ Al_2O_3 , an increase in peak intensity can be analyzed. Particle size increased from 2.5 in $\gamma-Al_2O_3$ to 16.2 nm in 20%-CuO/ $\gamma-Al_2O_3$. However, this increment in particle size is not too much to affect the crystalline integrity of $\gamma-Al_2O_3$ matrix. The additional broadness of diffraction peaks at lower copper percentages is dedicated to more amorphous phase of composites [46].

Figure 2. X-ray diffraction patterns (a) and Fourier-transform infrared (FTIR) spectra (b) of pure $\gamma-Al_2O_3$ and CuO/Al_2O_3 nanomaterials.

Debye-Scherrer formula was used to estimate the average crystallite size, Equation (4):

$$D_{av} = K \cdot \lambda / (\beta \cdot \cos \theta) \quad (4)$$

Here, D_{av} is the average crystallite size in nm, λ is the wavelength of X-ray (1.5418 nm) while using Cu as an anode, θ is Bragg's angle and β is the full width of the diffraction peak at half of the maximum. The calculated crystallite size for CuO is 14.6 nm which lies in the range between 10 to 30 nm as already reported [47–50]. The crystallite sizes of alumina increase from 2.5 nm (for pure γ -Al₂O₃) to 16.2 nm (20%-CuO/ γ -Al₂O₃) as shown in Table 1. This increment in crystallite size was already observed in CuO/Al₂O₃ materials, which might be due to the insertion of CuO items into the crystal lattice of γ -Al₂O₃ [44]. In all samples, the CuO impregnation and calcination steps resulted in the increased crystallite size.

Table 1. Average crystallite size calculated from Scherrer formula.

Electrocatalyst	D_{av} (nm)
CuO	14.6
γ -Al ₂ O ₃	2.5
4%-CuO/ γ -Al ₂ O ₃	7.1
8%-CuO/ γ -Al ₂ O ₃	9.1
12%-CuO/ γ -Al ₂ O ₃	11.5
16%-CuO/ γ -Al ₂ O ₃	15.1
20%-CuO/ γ -Al ₂ O ₃	16.2

Fourier-transform infrared (FTIR) spectra of all materials were obtained by using Nicolet 5PC, Nicolet Analytical Instrument Protea, Cambridgeshire, UK and compared with that of the bare CuO in Figure 2b. The absorption signals at ~500, ~1300 and ~1670 cm^{−1} indicate the stretching vibration of the Cu–O bond [51]. This analysis further confirms the successful impregnation of CuO into γ -Al₂O₃ support. Our results indicate that, at low copper loadings (below 10%), Cu²⁺ ions form a well-dispersed interaction species with the support. At high copper loadings (after saturation of the support, i.e., >16% Cu), segregation of bulk-like CuO occurred. The crystallite size of this CuO phase increases with metal loading [52].

3.2. Surface Characterization

The surface morphology, porosity and effect of CuO impregnation on the textural nature of Al₂O₃ in all synthesized materials were investigated by scanning electron microscopy (SEM) using TESCAN (Brno, Czech Republic) MAIA3, i.e., an ultra-high-resolution SEM. As displayed in Figure 3, γ -Al₂O₃ showed plate-like morphology with large pores (Figure 3a–c at different magnifications) and significant dendrites distributed over the surface similar to the earlier reports [53,54]. Interestingly, these plates were converted to a porous network-like structure when the contents of CuO were increased in materials as shown in Figure 3d–h). The CuO nanoparticles are heterogeneously distributed on the surface of Al₂O₃ nanostructures. The energy dispersive spectrum corresponds to the presence and elemental purity of Al, Cu and O, as displayed in Figure 3h.

Figure 3. SEM micrographs for pure Al_2O_3 at 20 μm (a), 5 μm (b) and 2 μm (c) and for 4%–20%–CuO/ γ - Al_2O_3 materials respectively at 1 μm (d–h) and (i) Energy dispersive spectrum for 4%–CuO/ γ - Al_2O_3 .

Low-magnification TEM nanostructures shown in Figure 4a–f are taken using TEM, JEOL 2100F (Tokyo, Japan), 200 kV to assess the surface picture of as-synthesized γ - Al_2O_3 and 16%–CuO/ γ - Al_2O_3 matrices and if any agglomeration observed in the nanoparticles. TEM images for γ - Al_2O_3 shown in Figure 4 a and b displayed the globular structure of particles and the images corresponds with the already reported TEM nanostructures [55,56]. Figure 4c–f represents the TEM images for 16%–CuO/ γ - Al_2O_3 and it is evident that incorporation of CuO into γ - Al_2O_3 matrix alters the surface structure. The modification in the γ - Al_2O_3 structure and a reconstructed composite surface is associated with dispersion of fine metal particles in catalysts [56]. Also, it can be perceived that the composite oxide is assembled from nearly uniform particles exhibiting similar shape, and significant porosity,

and no big blocks are observed [57]. In such catalysts, CuO dispersed on the surface of the flake-like γ -Al₂O₃ generate synergy and coupling effects for ammonia adsorption [58].

Figure 4. TEM images for pure Al₂O₃ at 300 nm (a), 500 nm (b), and for 16%-CuO/ γ -Al₂O₃ materials at 500 nm (c), 100 nm (d), 50 nm (e) and 5 nm (f).

3.3. Electrochemical Impedance Spectroscopy EIS

The electron transfer properties of all as-prepared nano-electrodes were studied via EIS in 1 M NH₃ and 0.1 M KOH. The Nyquist plots witnessed for CuO/ γ -Al₂O₃ modified glassy carbon electrodes are displayed in Figure 5, and associated EIS parameters are tabulated in Table 2. Systematically, the electron transfer resistance decreased with increase in copper content while again undergoing a decrease after an optimum composition. It endorsed that 16% CuO/ γ -Al₂O₃ is optimal for electrochemical catalysis. A significantly lower value of R_{ct} referred to the superior conductivity and much efficient electrocatalytic activity of 16%-CuO/ γ -Al₂O₃, comparative to other composites of the series. The differences in electrochemical behavior of the as-synthesized electrocatalysts depend upon the relative feasibility of electron transferal [26].

The nature of electrodes exhibits no influence on solution resistance (R_s) and Warburg resistance (R_w) because these are features of electrolyte and diffusion of electroactive specie that are common in all observations. However, the charge-transfer resistance (R_{ct}) and constant phase element (CPE) are influenced by modification of electrodes, as they are associated with conductive properties of the active material. α represents capacitance and surface roughness, respectively and its value varies from 0 to 1. Herein, currently modified electrode systems have α value ranging from 0.56 to 0.87, revealing that catalysts depicted enough surface roughness, which also correlates with the SEM and TEM observations. The electron-transfer rate constant k_{app} for as-proposed catalysts was calculated by Equation (5) [59].

$$k_{app} = RT/F^2 \cdot R_{ct} \cdot C \quad (5)$$

Here, F represents the Faraday's constant, C corresponds to concentration of analyte and R is universal constant in SI units. It is obvious from Table 2 that the value of k_{app} for 16%-CuO/ γ -Al₂O₃ is greatest among the series of nanomaterials, referring to its highest capacity to assist the AEO reaction.

Figure 5. Electrochemical impedance spectroscopy (EIS) spectra for 4%–20%-CuO/ γ -Al₂O₃ electrodes recorded in 1 M NH₃ + 0.1 M KOH aqueous solutions. Inset represents the model fit for calculating parameters.

Table 2. Parameters estimated from EIS analysis of electrocatalysts.

Electrocatalysts	R _s (Ω)	R _{ct} (kΩ)	CPE (μF)	α	W _o (Ω)	k _{app} /10 ^{−9} (cms ^{−1})
4%-CuO/ γ -Al ₂ O ₃	816.0	23.92	2.57	0.80	17.0	10.4
8%-CuO/ γ -Al ₂ O ₃	770.6	22.7	2.12	0.87	16.7	8.81
12%-CuO/ γ -Al ₂ O ₃	968.0	22.2	2.26	0.82	16.0	10.8
16%-CuO/γ-Al₂O₃	736.0	3.92	55.4	0.56	13.9	61.2
20%-CuO/ γ -Al ₂ O ₃	934.2	27.9	4.77	0.84	23.6	8.73

3.4. Active Surface Area of the CuO/ γ -Al₂O₃ Modified Electrodes

The electrochemical active surface area (ECSA) of a catalyst is an important performance indicator of any electrochemical reaction; therefore, cyclic voltammograms of all prepared electrocatalysts were recorded in a standard redox solution (5.0 mM K₄[Fe(CN)₆] + 3 M KCl) at 100 mVs^{−1} for ECSA estimation. Peak current (i_p) increment with CuO contents in the observed CV profile corresponded to a reversible one-electron transfer process using the synthesized nanomaterials as electron mediators in modified electrodes in K₄[Fe(CN)₆] electrolyte (Figure 6a). This observation of a reversible CV profile points to the facile electro kinetics in the model redox couple, which correlates the electrocatalytic behavior of the used materials. The peak currents corresponding to [Fe(CN)₆]^{4−} oxidation and peak current of [Fe(CN)₆]^{3−} reduction increase with the increase in the concentration of active CuO thus overall a diffusion-controlled process [60]. The ECSA of electrodes was calculated by applying the Randles-Sevcik Equation (6) [26].

$$i_p = 2.69 \times 10^5 \cdot n^{3/2} \cdot A \cdot D^{1/2} \cdot \nu^{1/2} \cdot C \quad (6)$$

Figure 6. Cyclic voltammetric profiles on 4%–20%–CuO/γ-Al₂O₃ modified electrodes materials in (5.0 mM K₄[Fe(CN)₆] + 3.0 M KCl) solution at scan rate of 100 mV·s⁻¹ (a) and comparison of ECSA (b), Comparison of AEO in 0.1 M KOH + 1.0 M NH₃ at 100 mV·s⁻¹ (c) and 16%-CuO/γ-Al₂O₃ with bare CuO and γ-Al₂O₃ (d).

Here, i_p is the peak current, n is the number of electrons transferred, A is the electrochemical active surface area (cm²), D is the diffusion coefficient (0.76×10^{-5} cm²·s⁻¹ at 25 °C), [61] v is the scan rate (V·s⁻¹) and C is the concentration of the analyte. ECSA of catalysts are compared in Figure 6b that increases in the following order: 4%-CuO/γ-Al₂O₃ < 8%-CuO/γ-Al₂O₃ < 12%-CuO/γ-Al₂O₃ < 20%-CuO/γ-Al₂O₃ < 16%-CuO/γ-Al₂O₃. This little drop in ECSA of 20%-CuO/γ-Al₂O₃ may affect from the agglomeration and consequent phase-out of CuO nanoparticles at its higher loading.

3.5. Electrochemical Studies

Electrocatalytic responses of all CuO/γ-Al₂O₃ materials towards ammonia electro-oxidation (AEO) was investigated by cyclic voltammetry in 1.0 M NH₃ and 0.1 M KOH as displayed in Figure 6c,d. The peaks observed in both the forward (anodic) and reverse (cathodic) scans correspond to oxidative and reductive removal of chemisorbed species of ammonia, respectively [62]. The height of the anodic peak represents the electro-oxidation of ammonia on the surface of the electrodes. The anodic peak current increases with CuO contents in CuO/γ-Al₂O₃ nanomaterials; however, 16%-CuO/γ-Al₂O₃ shows the best performance towards AEO compared to other serial materials (Figure 6c), bare CuO and γ-Al₂O₃ (Figure 6d). The onset potential for AEO is found to be about −0.35 V vs. Ag/AgCl (i.e., −0.2 V vs. NHE) which is comparable to the Pt electrode [5,63–65].

To examine the electrode kinetics and the I–V responses towards AEO, voltammograms were also recorded for each catalyst at various scan rates from 10 to 100 mV·s⁻¹. As shown in Figure 7a–e, a linear increase in peak current of AEO at ~0.2 V is observed with a scan rate that indicates a facilitated electron transfer process of ammonia electro-oxidation. Therefore, the proposed nanocatalysts behave like the adsorptive species on the electrode surface [9]. The electrochemical response of each material towards AEO was enhanced with varying contents of active component, i.e., CuO in CuO/γ-Al₂O₃. This further confirms

that CuO species present at the surface of catalysts play important role in AEO, more active sites available at the surface will maximize the ammonia adsorption thus leading to AEO high performance. The AEO strongly depends on the adsorption/desorption of NH_3 species and the number of available active sites of active components at the surface of the electrode [66]. Similarly, two peaks in the cathodic curve are attributed to desorption of ammonia and proton at the surface of the catalysts, Figures 7 and 8 [67]. The first cathodic peak is attributed to the reduction of reaction intermediates. Besides, the anodic and cathodic peak currents are also increased with the number of available active sites due to CuO. An anodic shoulder peak at -0.4 V can be attributed to the structural sensitivity of catalysts towards oxidation of pre-adsorbed hydrogen or nitrogen-containing intermediates at the surface of the electrode [68]. However, the anodic shoulder peak is suppressed by the ammonia oxidation peak when the contents of CuO are increased from 4% to 20% while the cathodic shoulder peaks increase because of the conversion/reduction of reaction intermediates. In this way, it can be said that irreversibility character increases with an increase in copper content up to an optimum level. As observed in Randles-Sevcik plots (Figure 7f), the peak current (i_p) exhibits a linear relationship with the square root of scan rate ($v^{1/2}$), which is an indication of a diffusion-controlled process for AEO [67,68].

Figure 7. Cyclic voltammograms for 4%–20%-CuO/γ-Al₂O₃ recorded in (1.0 M NH₃ + 0.1 M KOH) solution; scan rate from 10–100 mV s⁻¹ (a–e) and Randles-Sevcik plots derived from cyclic voltammetry (CV) curves of each catalyst (f).

Figure 8. Comparison of CV curves for 16%-CuO/γ-Al₂O₃ recorded pure 0.1 M KOH and solution of 1.0 M NH₃ in 0.1 M KOH (a), Multiple cycles for 20%-CuO/γ-Al₂O₃ (b), Comparison of NH₃ free voltammetry for 12%-CuO/γ-Al₂O₃ (c) and Comparison of 12%-CuO/γ-Al₂O₃ with bare glassy carbon electrode (d).

ECSA can be affected by the change of electrode layer structure; thus, 16%-CuO/γ-Al₂O₃ shows a higher peak current output than 20%-CuO/γ-Al₂O₃. After a certain limit, a further increase in CuO percentage leads towards agglomeration. Also, more ammonia molecules lead to an increase in diffusion-layer thickness, which results in a lower catalytic response in 20%-CuO/γ-Al₂O₃ [69]. The 16%-CuO/γ-Al₂O₃ is inferred to be the optimal loading of CuO for AEO under the optimal conditions. Subsequently, compositions above 20%-CuO/γ-Al₂O₃ were not studied to avoid the agglomerated material, as depicted by ECSA. Also, the same composition has been proved as the promising optimal loading of CuO onto γ-Al₂O₃ support for glucose sensing and methanol electro-oxidation [26].

To further assess the electrochemical activity of catalysts towards AEO, the electrochemical response of 16%CuO/γ-Al₂O₃ electrode was profiled by recording the cyclic voltammograms in pure 0.1 M KOH and 1.0 M NH₃ solution. As displayed in Figure 8, no significant oxidation peak current is observed in 0.1 M KOH compared to 1.0 M NH₃ as an analyte. This endorses the theory that the major peak corresponds to ammonia electro-oxidation rather than the electrolyte at the electrode surface [70]. The optimal onset potential for AEO is −0.35 V and the maximum oxidation peak current is observed at ~0.1 V. The electrochemical stability is a vital element in the commercialization of an electrocatalyst; therefore, it was determined by repeating CV cycles in 1.0 M NH₃ + 0.1 M KOH at 100 mV·s^{−1}. No significant current loss was observed after 10 CV cycles in Figure 8b, which indicates that the used catalysts give the stable performance towards AEO and can be commercialized for industrial applications. Concerning low CuO percentages, it is observed from Figure 8c that it also oxidizes ammonia to an extent, although current response is lower than that for high copper contents. Figure 8d gives a validation that a bare glassy carbon electrode when modified with 12%-CuO/γ-Al₂O₃, gave an oxidation

output. Hence, it can be inferred that even a small amount of CuO can electro-catalyze ammonia oxidation.

3.6. Diffusion Coefficients for AEO on CuO/ γ -Al₂O₃ Modified Electrodes

Diffusion coefficient (D) is an important parameter to study mass transfer kinetics, and it depends on various factors including analyte size and the concentration of electrolyte. Thus, the diffusion coefficients for ammonia (D_{NH_3}) in 0.1 M KOH were determined by applying the Randles-Sevcik formula (Equation (5)), which shows a linear relationship between the peak current and square root of the scan rate ($v^{1/2}$). The adsorption of ammonia occurs until the surface achieves saturation. Adsorbed nitrogen species cover and hence block the surface, whereas $\text{NH}_2(\text{ads})$ and $\text{NH}(\text{ads})$ seem to be the active species, which recombine to form N_2H_x ($x = 2-4$) species as reaction intermediates. These finally dehydrogenate to form N_2 . The recombination of NH_x species is proposed to be the rate-determining step [71]. Generalized from overall ammonia electro-oxidation reaction (Equation (3)), three electrons (i.e., $n = 3$) are required for AEO. Moreover, quite similar ammonia oxidation voltammograms are reported earlier, describing it as a three-electron process [72]. The D_{NH_3} using all the catalysts can be estimated from the slope of the Randles-Sevcik (i_p vs. $v^{1/2}$) plot at a constant scan rate ($100 \text{ mV}\cdot\text{s}^{-1}$) at 25°C [73]. Resultantly, 16%-CuO/ γ -Al₂O₃ gives the highest value of the diffusion coefficient as compared to the other materials Ni/Pt [65] and Ni/Ni(OH)₂ [18], as enlisted in Table 3. Usually, the diffusion coefficient for AEO in KOH electrolyte (10^{-9}) is much lower than that of water (2.4×10^{-5}) [66] due to the presence of hydroxyl (OH^-) ions in the electrolyte [20].

Table 3. Diffusion coefficients values for AEO using CuO/ γ -Al₂O₃ modified electrodes in 0.1 M KOH at 25°C .

Electrocatalyst	$D_{\text{NH}_3} \cdot 10^{-9} (\text{cm}^2\text{s}^{-1})$
4%-CuO/ γ -Al ₂ O ₃	1.0
8%-CuO/ γ -Al ₂ O ₃	2.6
12%-CuO/ γ -Al ₂ O ₃	2.7
16%-CuO/γ-Al₂O₃	4.1
20%-CuO/ γ -Al ₂ O ₃	3.8
Ni/Pt [55]	1.2
Ni/Ni(OH) ₂ [16]	2.8
Ionic liquids [16]	0.1

3.7. Estimation of Bandgap Values of CuO/ γ -Al₂O₃ for Ammonia Electro-Oxidation

The electrochemical bandgap (E_g) and frontier orbitals energy levels (E_{HOMO} and E_{LUMO}) are important factors to understand the electrical and electrochemical properties of any material [74]. Although it is difficult to quantify the exact values for bandgaps, it can be estimated from onset potentials, as is widely done in the literature [75–77]. As described in mathematical expressions (Equations (7) and (8)), the onset potentials of oxidation (anodic) curve, i.e., $(E_{\text{onset}})_{\text{ox}}$ and reduction (cathodic) curve, i.e., $(E_{\text{onset}})_{\text{red}}$ linearly correlate with energies of frontier orbitals, HOMO (E_{HOMO}) and LUMO (E_{LUMO}), respectively [78].

$$E_{\text{HOMO}} = -[(E_{\text{onset}})_{\text{ox}} + 4.4] \text{ eV} \quad (7)$$

$$E_{\text{LUMO}} = -[(E_{\text{onset}})_{\text{red}} + 4.4] \text{ eV} \quad (8)$$

Here, the onset potentials are calibrated regarding the saturated calomel electrode [79]. As presented in Table 4, the estimated bandgap narrows by increasing the copper contents in materials from 0.98 eV (4%-CuO/ γ -Al₂O₃) to 0.22 eV (16%-CuO/ γ -Al₂O₃), which results in maximizing the conducting properties. Also, the bandgap decreases with the increase of crystallite size due to the quantum confinement effect [80,81]. Furthermore, the conductive electrocatalysts let ample electrons speed up the electrochemical reactions [82,83]. Therefore, in general, the materials containing higher CuO contents give better AEO per-

formance due to the rapid transfer of electrons from the conduction band. Accordingly, the most conductive response is provided by the catalyst of optimal composition, i.e., 16%-CuO/ γ -Al₂O₃.

Table 4. Electrochemical bandgap values derived from onset potentials vs. sat'd calomel electrode for AEO on the CuO/ γ -Al₂O₃ materials.

Catalyst	E _{(ons)oxi} (V)	E _{(ons)red} (V)	E _{HOMO} (eV)	E _{LUMO} (eV)	E _g (eV)
4%-CuO/ γ -Al ₂ O ₃	−0.64	−0.25	−3.16	−4.14	0.98
8%-CuO/ γ -Al ₂ O ₃	−0.43	−0.13	−3.56	−4.31	0.75
12%-CuO/ γ -Al ₂ O ₃	−0.53	−0.21	−3.98	−4.69	0.71
16%-CuO/γ-Al₂O₃	−0.41	−0.18	−3.90	−4.20	0.22
20%-CuO/ γ -Al ₂ O ₃	−0.32	−0.06	−3.89	−4.30	0.41

4. Conclusions

The copper oxide modified γ -Al₂O₃ electrocatalysts (CuO/ γ -Al₂O₃) were synthesized by the facile co-impregnation and calcination process. The CuO nanocrystals were successfully grown on γ -Al₂O₃ supports, as depicted by X-ray diffraction and FTIR. The shape of γ -Al₂O₃ support was changed from irregular to network-like by increasing the CuO contents, as observed in SEM images. The network-like structures coincided with the electrochemical active surface areas (ECSAs), which also varied with the CuO contents. The surface coarseness and homogeneity were seen in TEM images. Electrochemical characterization involved cyclic voltammetry and EIS that conferred to the absolute catalytic behavior of as-proposed electrocatalysts. The maximum ECSA and minimum charge-transfer resistance have been displayed by 16%-CuO/ γ -Al₂O₃, which makes it the optimal composition. The effect of CuO contents was investigated in the catalytic performance of ammonia electro-oxidation (AEO) in alkaline media. It was observed that the AEO is an irreversible and diffusion-controlled process under alkaline conditions on the surface of CuO/ γ -Al₂O₃ electrodes. Additionally, the suppressing of catalysts by nitrogenous species can be significantly reduced by increasing the CuO contents, as displayed by the continuous disappearance of anodic shoulder peak from lower to higher CuO loading. The successive increment in diffusion coefficients for NH₃ with increasing CuO to γ -Al₂O₃ ratio showed that these materials can effectively electro-oxidize the NH₃ due to facile electron transfer. Correspondingly, the prepared electrocatalysts demonstrated good electrocatalytic activity, reproducibility, and stability towards the ammonia electro-oxidation. Recent investigation of CuO/ γ -Al₂O₃ electrocatalysts has revealed a large synergistic effect towards AEO at ambient temperatures. Therefore, these nanomaterials could be used as efficient electrocatalysts or promoters in AEO due to the higher diffusion coefficient for NH₃, low bandgap, and chemical/electrochemical characteristics.

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