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Tin/Indium Electrodes for Liquid Ethanol Sensing at Various Concentrations

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ABSTRACT

Ethanol is widely used in medical, industrial and environmental sectors, prompting a growing demand for accurate and real-time detection technologies. However, conventional tin (Sn)-based ethanol sensors face major limitations, including low selectivity, poor stability and delayed response times, especially at higher ethanol concentrations. To address these challenges, this study aims to enhance the sensing performance of Sn electrodes by modifying them with indium (In) through an electrodeposition method at three concentrations: 0.01 M, 0.03 M and 0.05 M. The fabricated Sn/In electrodes were characterized and evaluated using chronoamperometry under different ethanol concentrations (25%, 50% and 95% v/v). Results revealed that the 0.05 M In-modified electrode achieved the highest current response (~0.75 mA) and response ratio (~600 Rt/Ro) at 95% ethanol. In comparison, the 0.03 M In electrode exhibited superior sensitivity at lower concentrations. All electrodes demonstrated rapid response times within two minutes of exposure. These findings suggest that indium-modified Sn electrodes are highly promising for liquid-phase ethanol sensing applications, offering enhanced sensitivity and tunability based on dopant concentration.

1. Introduction

Ethanol is a widely utilized volatile organic compound (VOC), with diverse applications in medical diagnostics, industrial manufacturing and environmental monitoring. However, prolonged or excessive exposure to ethanol, particularly in confined or poorly ventilated environments, can result

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in significant health risks and environmental hazards, as discussed by John *et al.,* [1]. Therefore, precise and real-time ethanol detection is essential in technologies such as breath analysers, fuel composition monitors, food quality sensors and industrial safety systems, as emphasized by Li *et al.,* [2]. This growing demand has driven substantial research into improving sensor selectivity, sensitivity and long-term stability.

Among the various sensing technologies, metal oxide semiconductor (MOS)-based ethanol sensors, especially those incorporating tin oxide (SnO_2), have gained attention due to their low cost, chemical durability and high sensitivity, as noted by Pandit *et al.,* [3]. These sensors operate by monitoring changes in electrical resistance when ethanol interacts with the metal oxide surface. Despite these benefits, traditional SnO_2-based sensors frequently exhibit limitations such as low selectivity, slow response and recovery times and signal saturation at elevated ethanol concentrations, as identified by Shi *et al.,* [4]. To address these challenges, researchers have focused on material modification strategies aimed at enhancing sensor performance.

One such strategy involves doping tin-based materials with elements like indium (In). As shown by Afrouzmehr *et al.,* [5], indium doping can improve surface catalytic activity, increase the density of oxygen vacancies and accelerate charge transfer processes, thereby enhancing ethanol adsorption and oxidation. Previous studies, including the work of Boroujerdi *et al.,* [6], have demonstrated that indium-modified Sn-based electrodes can provide superior selectivity and faster response times compared to undoped counterparts.

However, the efficacy of indium doping is strongly dependent on both the concentration and distribution of the dopant. Guo *et al.,* [7] have reported that low indium content (0.25–0.5%) improves carrier mobility and reduces response time, while moderate levels enhance catalytic performance. In contrast, Cai *et al.,* [8] found that excessive indium loading (>2%) may induce structural defects and nanoparticle agglomeration, which degrade overall sensor performance. These findings highlight the importance of precise control over indium content during electrode fabrication.

Electrodeposition (ED) has emerged as a practical and scalable technique for fabricating indium-doped tin electrodes. As described by Arulkumar *et al.,* [9], ED provides superior control over film thickness, dopant concentration and surface morphology compared to alternative methods such as chemical vapor deposition (CVD) or sol-gel techniques. Additionally, ED enables the production of rougher surfaces with higher active site densities, which are advantageous for gas sensing applications. The cost-effectiveness of indium-doped Sn electrodes also makes them a promising alternative to sensors based on noble metals like platinum or gold, as highlighted by Fu *et al.,* [10].

Nonetheless, challenges such as long-term signal drift, limited repeatability and reduced performance at high ethanol concentrations persist, as reported by Janith *et al.,* [11]. These unresolved issues underscore the need for further investigation into compositional tuning and advanced synthesis methods to develop reliable and efficient ethanol sensors.

Recent advancements in nanoscale material engineering—including doping and nanocomposite integration—have shown promise for enhancing sensor functionality. For example, Sanusi *et al.,* [12] demonstrated that incorporating graphene oxide (GO) into ZnO thin films significantly improves their optoelectronic and surface characteristics, making them more suitable for sensing and photovoltaic applications. Further improvements in structural, optical and electrical properties were achieved by optimizing the GO solution temperature during deposition in a study by Sanusi *et al.,* [13].

While notable advancements have been achieved in gas-phase ethanol sensors through material doping and nano structuring, the influence of indium doping on tin-based electrodes for liquid-phase ethanol sensing remains insufficiently explored. Most reported studies either examine alternative dopants or focus on gaseous ethanol detection, overlooking the specific role of indium concentration and electrodeposition parameters in liquid environments. This gap limits the optimization and

practical deployment of low-cost, high-performance sensors for biomedical and industrial applications. Therefore, this study is significant as it provides a systematic investigation into indium-modified tin electrodes fabricated via electrodeposition, aiming to evaluate their structural, morphological and electrochemical characteristics. The main objective is to develop sensitive, stable and cost-effective ethanol sensors capable of accurate detection across various liquid-phase ethanol concentrations.

2. Methodology

2.1 Materials and Electrode Fabrication

The fabrication of ethanol sensors in this study utilised high-purity reagents to ensure accuracy and reproducibility. Indium (III) chloride ($InCl_3$, Sigma-Aldrich, 99.999% trace metals basis) was chosen as the indium precursor due to its high purity and stability, essential for consistent and uniform electrodeposition, as reported by Deenadayalan *et al.,* [14]. Ethanol (95% purity, SYSTEM® ChemAR®) was used as the target analyte, simulating real-world detection scenarios relevant to industrial and medical applications, as used by Ran *et al.,* [15]. Acetone (ACS reagent grade, SYSTEM® ChemAR®) served as a cleaning agent to remove surface contaminants that may affect morphology and performance, similar to the approach by Hao *et al.,* [16].

Tin foil (99.99% pure, Sigma-Aldrich) was chosen as the substrate because of its established function in metal oxide-based ethanol sensing. To prevent any interference from ionic contaminants, deionized (DI) water was used to prepare all solutions. To ensure consistency among samples, the tin foil was sliced into 4 cm × 1 cm strips for electrode preparation. After extensively cleaning these strips with acetone and ethanol, they were rinsed with DI water to get rid of any remaining organics and surface oxides that might have affected their sensitivity and stability. To guarantee experimental uniformity, all compounds were of analytical quality and utilized without additional purification.

2.2 Electrodeposition of Indium onto Tin Electrodes

Electrodeposition (ED) was employed to modify the Sn electrodes, offering precise control over dopant concentration and morphology, factors that are critical for enhancing ethanol sensing properties, as noted by Ran *et al.,* [15]. A 0.1 M indium chloride stock solution was prepared by dissolving 2.2 g of $InCl_3$ in 100 mL of deionized water with constant stirring. This solution was then diluted to prepare 0.01 M, 0.03 M and 0.05 M concentrations to investigate the effect of indium loading on sensor performance.

The ED process was conducted in a two-electrode configuration, using the Sn electrode as the cathode and a platinum wire as the anode. Deposition was carried out at 1.5 V for 10 minutes at room temperature, based on prior optimization studies showing that longer durations may lead to agglomerated or uneven films that reduce performance, as explained by Hao *et al.,* [16]. After deposition, the Sn/In electrodes were rinsed with deionized water to remove unreacted precursors and residual ions. Figure 1 illustrates the electrodeposition process involving two Sn electrodes.

To promote strong film adhesion and form a protective ultrathin SnO_2 layer, the electrodes were dried in an oven at 90 °C for one hour. This low-temperature annealing process stabilizes surface morphology and reduces defect formation, contributing to improved selectivity and device longevity. A study by Muthukrishnan *et al.,* [17] found that low-temperature deposition of SnO_2 ETLs, combined with oxygen plasma treatment, significantly enhanced film quality and device efficiency from 2.3% to 15.3% by improving wettability and increasing perovskite grain size, demonstrating the potential of low-temperature processing for flexible perovskite solar cells.

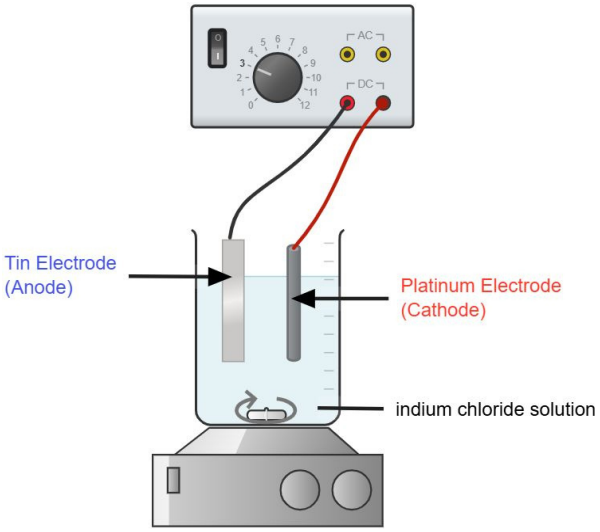


Fig. 1. Schematic diagram for the ED process

2.3 Electrochemical Testing using Chronoamperometry (CA)

Chronoamperometry (CA) was employed to evaluate the real-time electrochemical response of the Sn/In electrodes, as this technique allows precise monitoring of current fluctuations under a constant applied potential. This approach aligns with methods used in recent studies on ethanol oxidation electrocatalysts. A three-electrode system was used, consisting of a Sn/In working electrode, an Ag/AgCl reference electrode and a platinum counter electrode, a configuration found by Abdo *et al.,* [18] to provide stable and accurate electrochemical measurements for similar sensing applications.

Ethanol solutions at concentrations of 25%, 50% and 95% v/v were prepared to investigate the sensor's performance across varying exposure levels. CA measurements were conducted at a fixed potential of 10 V for 10 minutes at room temperature. The resulting current–time curves were analysed to determine sensitivity, stability and response time, as demonstrated in a study by Lović *et al.,* [19], which highlighted the effectiveness of this approach for evaluating electrochemical sensor performance.

In addition to current measurements, resistance-based tests were also conducted to calculate the response ratio, as shown in Eq. (1):

$$\frac{Rt}{Ro} \tag{1}$$

where Rt represents the resistance at a specific ethanol concentration and Ro is the baseline resistance in air or at 0% ethanol. This ratio reflects the electrode's oxidation efficiency and electron transport properties. Based on these results, the optimal indium concentration for achieving maximum sensitivity and reproducibility was identified. A schematic diagram of the three-electrode electrochemical setup is shown in Figure 2.

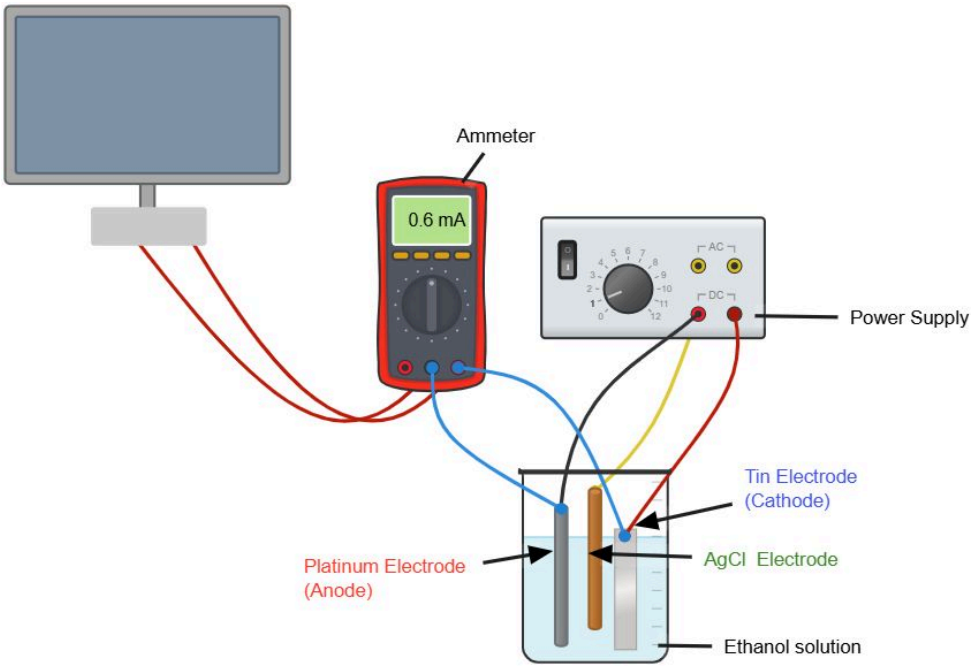


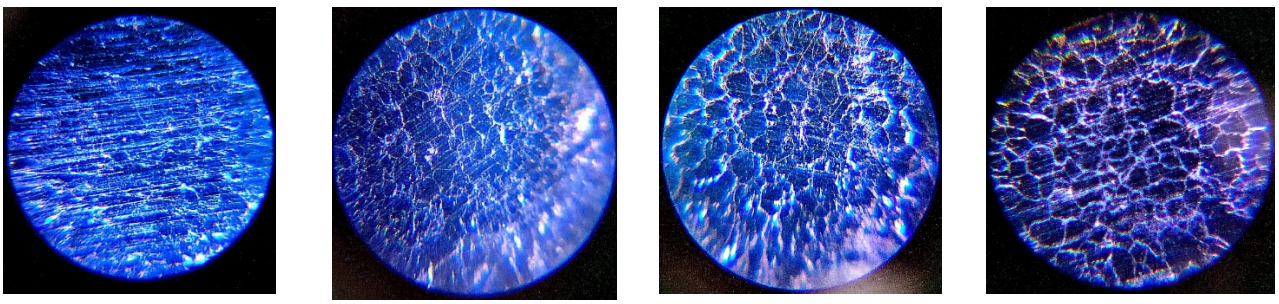
Fig. 2. Schematic diagram for a three-electrode electrochemical cell for ethanol liquid sensing

3. Results

3.1 Surface Morphology

Figure 3 shows the surface morphology of Sn/In electrodes with different indium concentrations, observed using an optical microscope (60×180× zoom). The unmodified Sn electrode (Figure 3(a)) exhibited a smooth and flat surface with minimal porosity, which indicates a limited number of active sites for ethanol oxidation. As the In concentration increased, the surface roughness and porosity also increased (Figures 3(b) to 3(d)). The 0.05 M Sn/In electrode displayed the highest surface roughness and porosity, which are advantageous for ethanol adsorption and electron transfer efficiency.

This trend is consistent with previous research showing that increased surface roughness enhances the interaction between the sensing surface and ethanol molecules, improving sensor responsiveness, as observed by Razalli *et al.,* [20]. Additionally, higher porosity is associated with a greater density of catalytically active sites, which improves charge transfer in metal-oxide-based sensors, as supported by Costa *et al.,* [21] and Dutta *et al.,* [22].

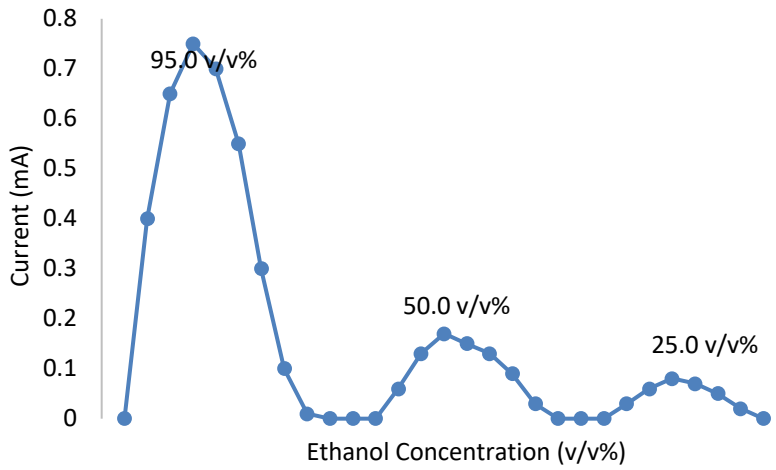


(a) (b) (c) (d)

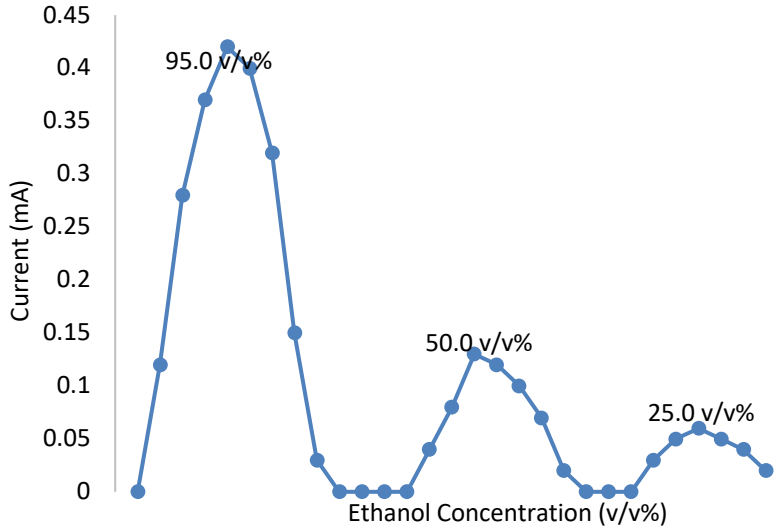
Fig. 3. Optical microscope images of (a) unmodified Sn electrodes and modified with (b) 0.01 M In, (c) 0.03 M In (d) 0.05 M In

3.2 Ethanol Liquid Sensor Measurement

The response curves of Sn/In sensors with varying indium compositions (0.05 M, 0.03 M and 0.01 M) were analysed after exposure to ethanol at concentrations of 25%, 50% and 95% v/v. As shown in Figure 4, the current response increased with higher ethanol concentration across all electrode types. The 0.05 M Sn/In electrode (Figure 4(a)) showed the highest peak current, followed by the 0.03 M (Figure 4(b)) and 0.01 M (Figure 4(c)) electrodes.



(a)



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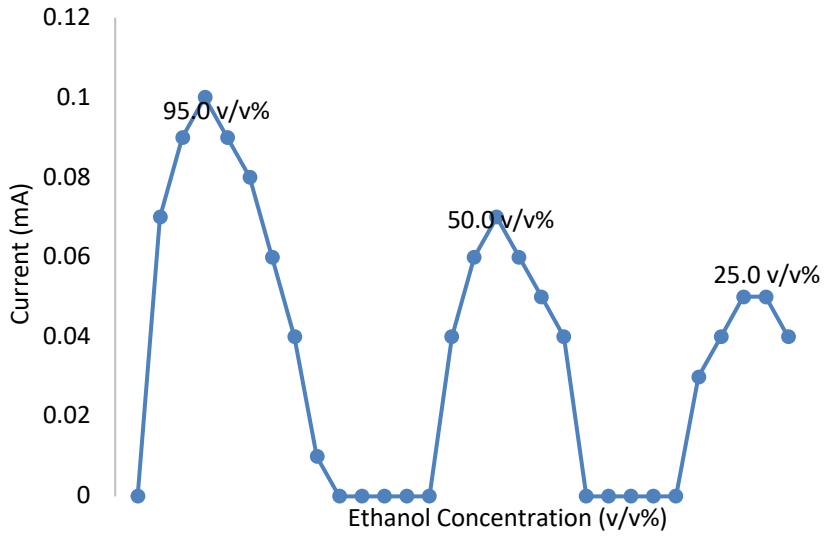


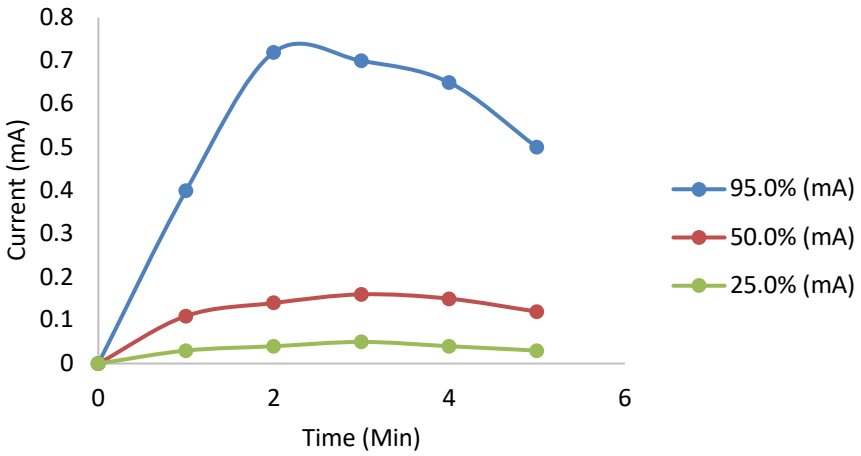
(c)

Fig. 4. The response curve of the (a) 0.05M Sn/In (b) 0.03M Sn/In (c) 0.01 M Sn/In electrode sensor upon exposure to ethanol liquid at different concentrations. The concentration varied from 95 v/v% to 25 v/v%

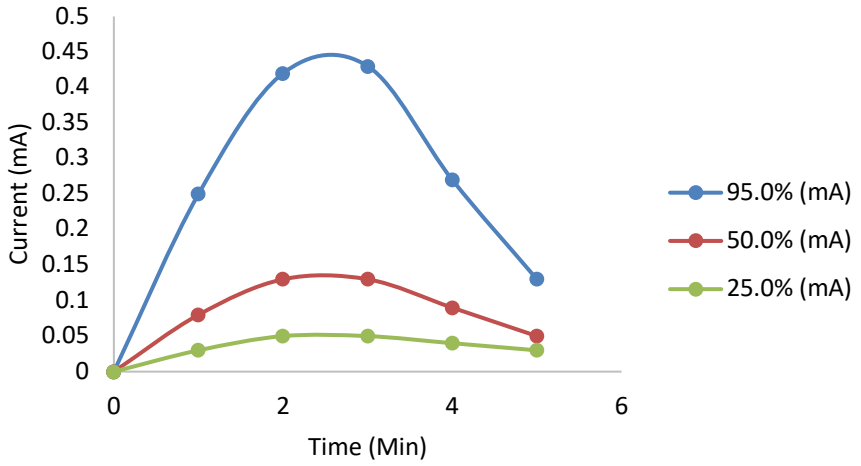
This behaviour indicates that indium doping significantly improves the electrocatalytic activity for ethanol oxidation, which correlates with increased current generation. Berwal *et al.,* [23] reported similar findings, where increased metal content in Sn-based electrodes led to improved conductivity and enhanced sensor response. Dadkhah *et al.,* [24] also demonstrated that Sn-based electrodes with higher metal loadings exhibit better charge transfer performance and sensitivity.

The synergistic effects between Sn and In further enhance ethanol oxidation by improving electron mobility and lowering activation energy. Goel *et al.,* [25] confirmed that the Sn/In alloy system supports fast charge transfer, while Kong *et al.,* [26] found that Sn/In combinations also enhance overall sensor selectivity. Conversely, reduced indium content leads to fewer active sites and weaker response, as reported by Saruhan *et al.,* [27].

Figure 5 illustrates the current response over a 5-minute duration, where the 0.05 M Sn/In electrode reached a peak of approximately 0.75 mA, followed by ~0.45 mA for the 0.03 M electrode and ~0.10 mA for the 0.01 M electrode. All electrodes exhibited a rapid rise in current within the first two minutes, reflecting fast ethanol adsorption and oxidation. After electrode removal, a gradual current decline was observed due to reduced ethanol interaction. This behaviour is consistent with reports by Goel *et al.,* [25], who noted a current drop-off when ethanol supply ceased.



(a)



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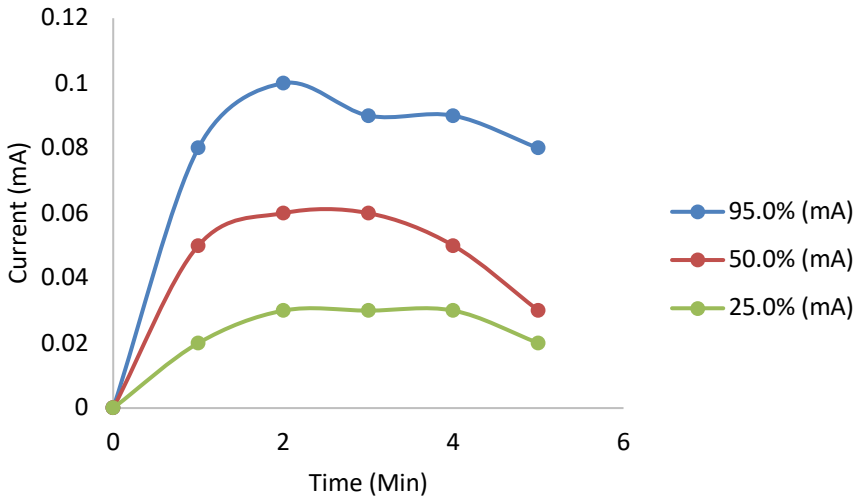


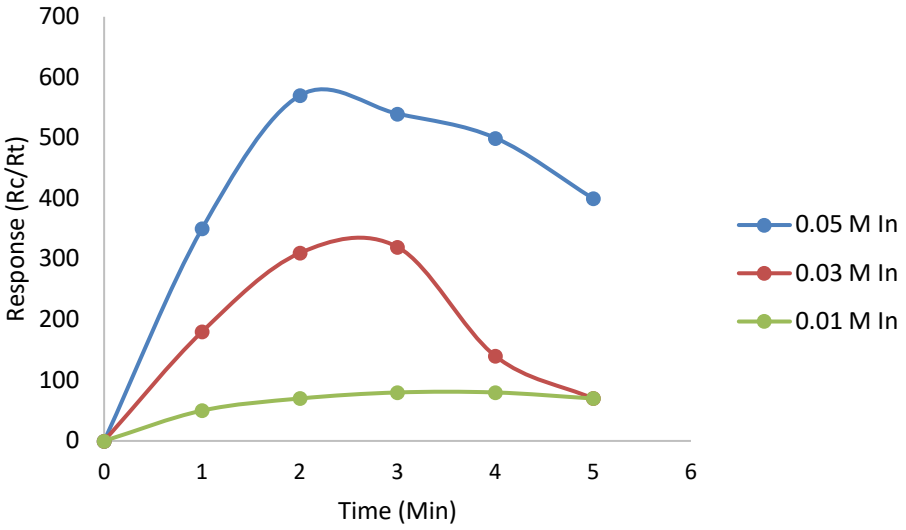
(c)

Fig. 5. The current (mA) of Sn electrode modified with (a) 0.05M (b) 0.03M (c) 0.01M of indium for an ethanol sensor at different concentrations and reaction times (min)

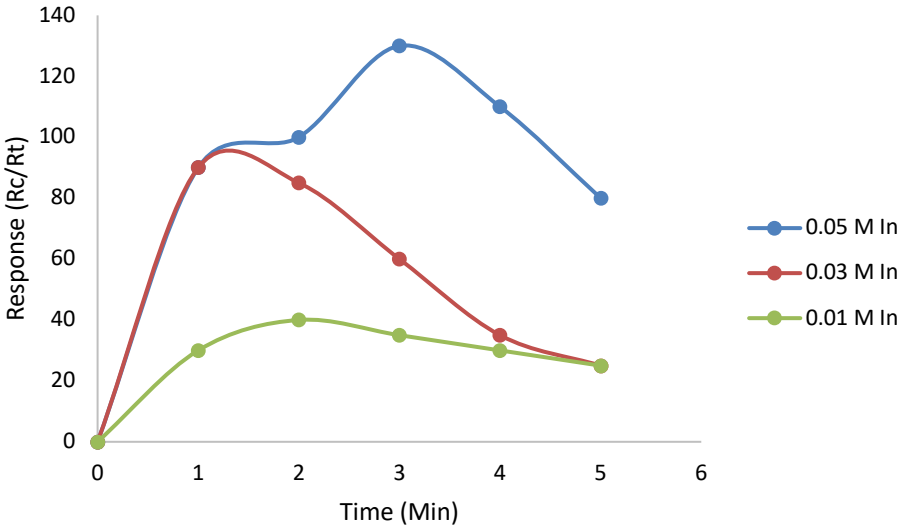
Figure 6 shows the resistance-based sensor response (Rt/Ro) of Sn/In electrodes at various ethanol concentrations (95%, 50% and 25% v/v) over a 5-minute testing period. At 95% ethanol, the 0.05 M In electrode exhibited the highest response ratio (~600), followed by the 0.03 M (~300) and 0.01 M (~100) electrodes. Similar patterns were observed at 50% and 25% ethanol concentrations, although at the lowest concentration, the 0.03 M electrode showed better performance than the 0.05 M electrode.

This result suggests that moderate doping (0.03 M) optimizes ethanol interaction and sensor response under low ethanol concentrations, likely due to balanced catalytic activity and minimized side reactions. Similar conclusions were drawn by Dutta *et al.,* [22], who emphasized the importance of dopant level optimization. Kong *et al.,* [26] also noted that excessive indium may hinder sensing efficiency by inducing side reactions or surface saturation.

Overall, the findings indicate that indium content and ethanol concentration jointly influence the sensor's responsiveness, selectivity and stability.



(a)



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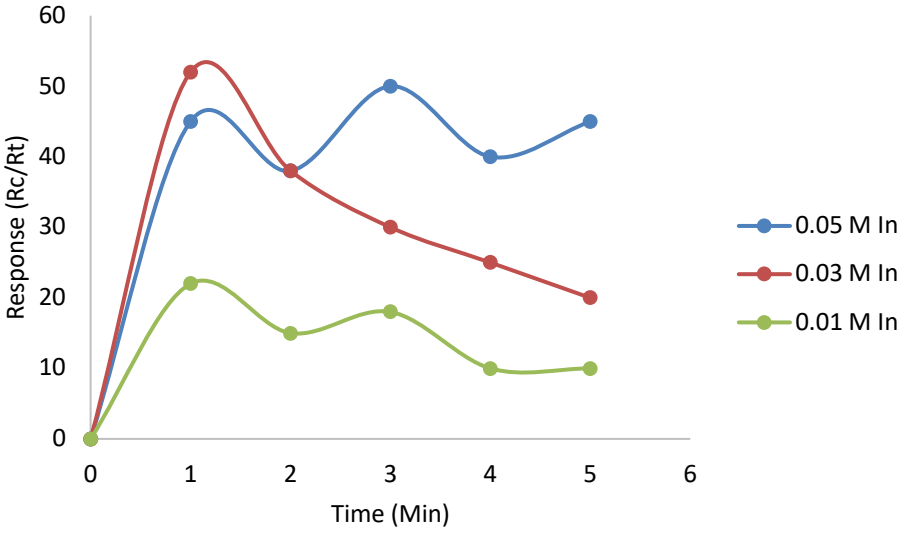

(c)

Fig. 6. Response of different indium modifications on Sn electrodes as ethanol sensors at (a) 95.0 v/v% (b) 50.0 v/v% (c) 25 v/v% of ethanol concentration and various reaction times (min)

4. Conclusions

This study successfully demonstrated that modifying tin electrodes with indium via electrodeposition significantly improves their performance in liquid-phase ethanol sensing. Among the samples tested, the electrode doped with 0.05 M In achieved the highest current response (~0.75 mA) and resistance response ratio (~600 Rt/Ro) at 95% ethanol. This enhanced performance is attributed to increased surface roughness, porosity and catalytic activity.

Interestingly, the 0.03 M In electrode showed better sensitivity at lower ethanol concentrations (25% v/v), indicating that moderate indium content provides a more balanced surface for ethanol oxidation. All electrodes displayed fast response times within the first two minutes of exposure, though a gradual current decline occurred after removal from ethanol, likely due to surface passivation.

These results suggest that careful control of indium concentration during fabrication can fine-tune the performance of Sn-based ethanol sensors. Future work should explore long-term durability, nano structuring techniques and integration into flexible or real-time sensing platforms for use in biomedical and industrial applications.

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