

The Effect of Saccharin on SnNi Alloy: the Electrodeposition and its Electrocatalytic Activity in Ethanol Oxidation Reaction

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Abstract

The development of Direct Ethanol Fuel Cell (DEFC) has attracted much attention, as alternative energy sources due to its various advantages. However, among its various advantages, DEFC has several problems, such as the kinetics of the ethanol oxidation reaction. Transition metal-based catalysts such as nickel and tin are considered as potential catalysts for DEFC due to their oxophilic properties that can improve catalytic activity. In this study, the effect of saccharin on SnNi bimetallic alloy catalyst synthesized by electrodeposition method on copper wire substrate was investigated. SnNi samples were characterized by several techniques, including X-ray diffraction, Scanning electron microscopy, and energy dispersive X-ray spectroscopy. Saccharin addition had a significant effect on the morphology, crystallite size, and composition of the catalyst. The presence of saccharin causes the formation of more uniform particles and has a smaller size. The sample with the addition of saccharin had a smaller charge transfer resistance value 4.82Ω , lower tafel slope by 115 mV/dec , and show higher j_i/j_b ratio by 0.55 . Furthermore, as the current density decreases, the SnNi catalyst with saccharin has a slow decrease rate and higher stability than the SnNi catalyst without saccharin.

Keywords: electrodeposition, SnNi, electrocatalyst, ethanol electrooxidation

1. Introduction

Due to the scarcity of fossil fuels and the impact of greenhouse gas emissions, there is a growing necessity and demand for environmentally friendly alternative providers of renewable energy sources. Among the promising renewable energy technologies, high-efficiency energy conversion devices such as direct ethanol fuel cells (DEFCs) have attracted considerable attention and are being widely developed due to their numerous advantages, they have low toxicity, high energy conversion efficiency, high power density and also have easy storage and handling [1]

Compared to other alcohol-fuel cells, such as methanol, DEFCs are preferred due to their low toxicity and also their abundant availability, as they are easily reproduced from agricultural waste or biomass [1-3]. Furthermore, ethanol possesses a higher energy density (8.00 kWh kg^{-1}) than methanol (6.10 kWh kg^{-1}) [2, 4]. This indicates that a greater quantity of energy can be derived from ethanol

relative to methanol, thereby reducing fuel consumption. DEFCs are capable of generating 12 electrons, which is twice the number generated by methanol oxidation in DMFC, which is 6 electrons for each complete oxidation reaction of alcohol to carbon dioxide [1–5]. However, the commercial utilization of DEFCs remains constrained by its low efficiency in converting chemical energy into electrical energy. This is attributed to the higher molecular complexity of ethanol in comparison to methanol, so DEFCs requires additional steps to break the C-C bond in a complete oxidation reaction [6]. Therefore, much research is still required to enhance the efficiency per mole of ethanol used in DEFCs.

One of the important components in DEFC is the electrode, which serves as the site for electrochemical reactions involved in the conversion of chemical fuel energy into electricity [7]. Therefore, the utilization of electrode materials, designated as electrocatalysts, with high catalytic activity is required to enhance the reaction

efficiency. To date, platinum (Pt) has been the most used element for ethanol oxidation reactions due to its high activity and relatively good stability [8]. However, its use as a catalyst is constrained by several factors, including its high cost and the Pt catalyst surface, which is susceptible to the poisoning of the CO intermediate during the reaction process, which decreases its catalytic activity and inhibits the reaction [9,10]. Therefore, various studies are still being conducted to identify potential materials that could replace noble metal-based catalysts, such as Pt. One promising avenue is the development of transition metal-based catalysts.

Nickel (Ni) is one of the transition metals that is abundant on earth and has low cost [11]. Compared with other non-noble metals, most Ni-based electrocatalysts show relatively high activity in the ethanol oxidation reaction [12]. Ni-based catalysts enable efficient ethanol oxidation reactions due to their high conductivity, thermal stability, and good electrical properties [13]. Nickel, especially in the oxidation state of Ni(III) as NiOOH, are highly electroactive during ethanol oxidation, which can improve the reaction efficiency [14,15]. However, alloying Ni with other metals produces synergistic effects that often result in superior catalytic performance compared to pure Ni [16–18].

Tin (Sn) can form useful alloys with many metals, including Ni [19]. Based on previous studies, SnNi alloys as catalysts have shown better stability compared to Ni/C, which could be due to the beneficial effects of Sn [20]. Sn is known to have higher oxophilicity, so the addition of Sn improves the oxophilic nature of the catalyst surface and reduces the poisoning of CO intermediates on the catalyst active sites [21,22]. Based on previous studies, discrete SnNi nanoparticles have been reported as stable electrocatalysts for methanol oxidation [23].

In addition to the composition of the catalyst, the morphology and size of the catalyst can also significantly affect its catalytic activity [19]. Increasing the surface area of deposited Ni-based electrocatalysts, either by reducing their size or increasing the number of nanoparticles by modifying their morphology, is known to improve the ethanol oxidation reaction [14]. The use of saccharin is known to be effective in improving the microstructure and smoothing the surface of the deposited material [24]. The addition of saccharin can increase the cathodic overpotential with an electrochemical system that increases the nucleation rate during deposition, thereby smoothing the grains and reducing the internal stress in some metal alloys, such as ZnNi and CoNi [25,26].

There are several techniques in the synthesis of SnNi alloys, but the synthesis of SnNi alloy nanoparticles by the

electrodeposition method and its application for the ethanol oxidation reaction is still rarely reported. Electrodeposition is one of the potential methods for the synthesis of various metal alloys because the process is simple, inexpensive, and has high efficiency and good control over the growth of alloyed metal particles [27]. In this paper, we have developed a SnNi nanoparticle alloy catalyst synthesized by the electrodeposition method and reported the effect of the presence of saccharin in the synthesis process on the morphological structure of the catalyst on its catalytic activity.

2. Materials and Method

2.1 Materials

Chemicals used for sample preparation and electrochemical measurement were nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) (Merck), Stannous Chloride (SnCl_2) (Merck), copper wire, boric acid (H_3BO_3) (Merck), ethanol ($\text{C}_2\text{H}_5\text{OH}$), Sodium Hydroxide (NaOH) (Merck), saccharin and aquadest. All chemicals were used as received without further purification.

2.2 Synthesis of SnNi electrocatalyst

Catalyst SnNi were synthesized using the electrodeposition method. The SnNi catalyst was synthesized with and without the addition of saccharin to investigate its effect on the properties and characteristics of the resulting catalyst. The inclusion of saccharin during the synthesis process was hypothesized to influence the morphology, crystallinity, and catalytic performance of the SnNi alloy.

The electrodeposition process is carried out in a three-electrode system with copper wire as the working electrode, Pt as the counter electrode, and Ag/AgCl as the reference electrode. A precursor solution was prepared by dissolving 0.09 M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 0.01 M SnCl_2 , 0.50 M H_3BO_3 , and 0.10 M H_2SO_4 . As a comparison, saccharin was added to the solution, to investigate the effect of saccharin on electrolyte solution. The deposition was carried out with electrodeposition method for 10 minutes on copper substrate with a potential of -1.40 V vs Ag/AgCl at room temperature. Before electrodeposition, the substrate was polished mechanically using sandpaper and washed with aquadest and ethanol. The obtained deposit was rinsed with distilled water and dried.

2.3 Characterization

The deposited samples were subjected to various analytical techniques for characterization. X-ray diffraction (XRD) was employed to identify the crystal phases present in the samples. Scanning electron microscopy (SEM) was

employed to analyze the surface morphology of the samples. Energy-dispersive X-ray spectroscopy (EDX) was used to determine the composition of the samples deposited on the copper wire.

2.4 Electrochemical test

Electrochemical measurements were performed in a standard three-electrode electrochemical cell using an electrochemical workstation, with Pt and Ag/AgCl used as the counter electrode and reference electrode, respectively. The copper wire substrate covered with the electrodeposited film served as the working electrode. Electrochemical impedance spectroscopy was used to determine the electron transfer resistance (R_{ct}) of samples. EIS analysis was measured at a frequency of 0.1 Hz – 100 kHz in 0.5M KCl solution. Cyclic voltammetry (CV) and Chronoamperometry (CA) measurements were performed to investigate the activity and stability of samples for ethanol electrooxidation. CV analysis was performed in 1 M NaOH and 0.1 M ethanol solution. The potential used is between -750 mV to 750 mV at a scan rate of 50 mV/s, starting from anodic current. Linear sweep voltammetry (LSV) curves were measured at a scan rate of 50 mV/s. The stability tests of samples were performed for ethanol electrooxidation with a constant potential of 0.3V vs Ag/AgCl for 120 minutes, utilizing a reaction vessel with a volume of 25 mL.

3. Results and Discussion

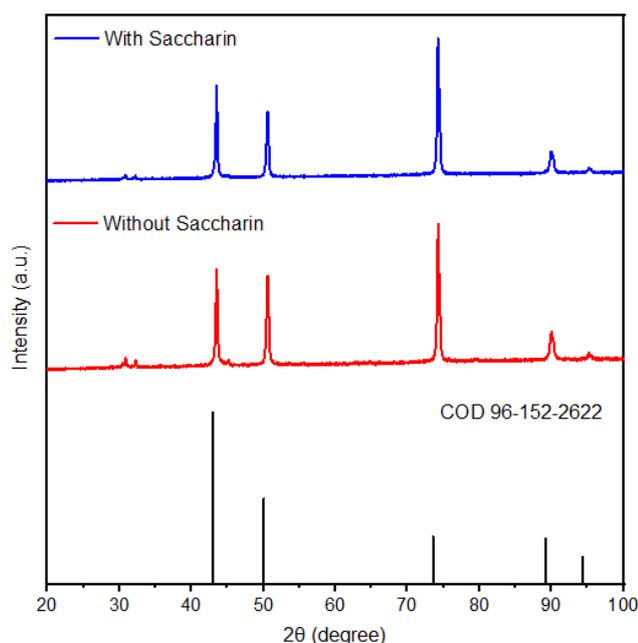


Figure 1. XRD diffraction pattern of SnNi alloy catalyst.

Both types of synthesized samples were characterized by the X-ray diffractometer. Figure 1 shows the diffraction pattern of the SnNi alloy catalyst. The diffraction patterns show peaks at 2θ 43.50° , 50.58° , 74.29° , 90.05° , and 95.28° corresponding to miller index of (111), (200), (400), (220), (311), and (222) respectively confirm the formation of single-phase SnNi alloy. The observed XRD pattern varies only in the peak position due to a slight shift. This is related to the difference in SnNi alloy composition of the two samples synthesized with and without saccharin addition. The crystallite size of the catalyst is computed using the Debye-Scherrer formula. The crystallite size of the SnNi with and without saccharin were found to be 27.30 and 28.26 nm, respectively.

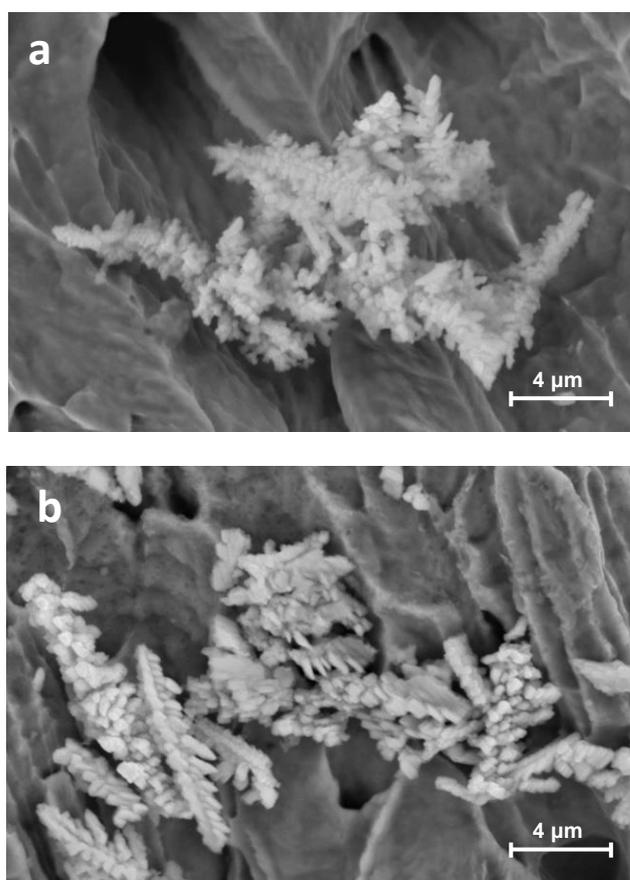


Figure 2. SEM images of electrodeposition SnNi (a) absence saccharin and (b) presence saccharin.

The crystallite size shows that the SnNi catalyst electrodeposited from the electrolyte containing saccharin has a smaller size than that synthesized without the addition of saccharin. The calculation results show that the SnNi catalyst electrodeposited from the electrolyte containing saccharin has a smaller size than that synthesized without the addition of saccharin. These results indicate that the presence of saccharin addition slows down the growth phase during SnNi deposition,

despite the high nucleation rate indicated by the small crystal size [26].

The morphology of the SnNi absence and presence of saccharin thin film synthesized through the electrodeposition method is shown in Fig. 2. According to the results, adding saccharin affects the morphology of the deposit. The morphology obtained is shaped like an oval circle and pointed on some particles. But in Fig. 2b the particle distribution is more uniform. This is due to the presence of saccharin in the electrolyte used. Saccharin is an additive that can repair the grain structure and enhance the quality of the deposited film, obtaining smoother, more compact, and brighter deposits [28]. This align with the results of research by Uhm et. al. [29], which demonstrated a decrease in surface roughness on Ni deposits along with the addition of saccharin concentration. The addition of saccharin as an additive to the electrolyte solution can improve the movement of electrons and electrical conductivity in the structure which will shift the reduction potential of metal ions to a higher one, resulting in a higher nucleation rate and has an effect on grain refinement [29,30].

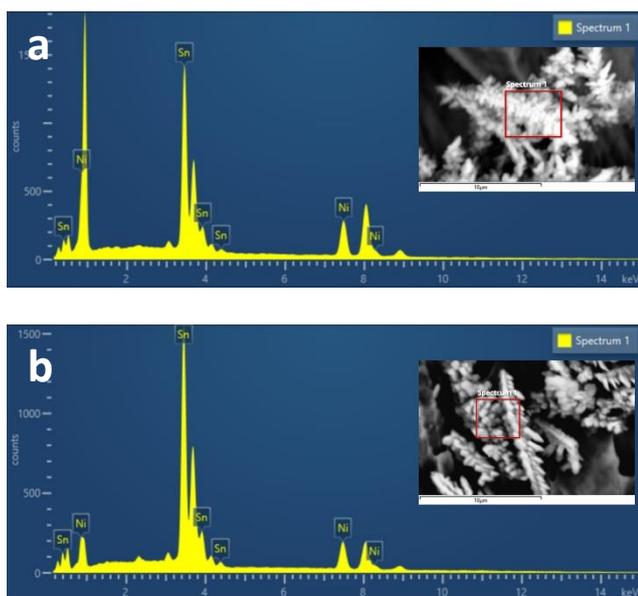


Figure 3. EDX spectrum of SnNi (a) absence saccharin, (b) presence saccharin.

EDX spectrum of SnNi with the presence saccharin and SnNi absence saccharin are shown in Fig. 3. EDX spectrum confirm the presence of Sn and Ni elements synthesized on copper wire substrates. The composition of Sn and Ni in the absence of saccharin and presence saccharin during deposition on copper wire are shown in Table 1. These EDX results verify that the synthesis of SnNi thin films with saccharin and SnNi thin films without saccharin has been formed on the substrate.

Table 1. Elemental composition (wt%) of SnNi in EDX

Sample	Elemental weight%	
	Sn	Ni
SnNi absence saccharin	78.19%	21.81%
SnNi presence saccharin	85.56%	14.44%

The presence of saccharin in the solution can inhibit precipitation due to its adsorption effect. The presence of saccharin tends to lower the Ni content and promote more anomalous behavior to a relatively small degree [31]. The EDX results of both samples show a greater percentage of Sn because Sn has a more positive standard reduction potential value, it can undergo reduction and be deposited at a potential of -1.40 V.

Table 2. The R_s and R_{ct} values measured using EIS technique.

Sample	R_s	R_{ct}
SnNi without saccharin	3.68 Ω	15.77 Ω
SnNi with saccharin	3.43 Ω	4.82 Ω

The Electrochemical Impedance Spectroscopy (EIS) measurements in 0.50 M KCl electrolyte with a frequency range of 100 kHz to 0.10 Hz. Aiming to determine the impedance of the system. The results are presented in a Nyquist plot which depicts the R_{ct} and solution resistance (R_s) values forming a semi-circle. This shape indicates the R_{ct} and the nature of the electrode interface [27]. The Nyquist plot of SnNi with saccharin and without saccharin is shown in Fig. 4, and the specific result of EIS has shows in Table 2.

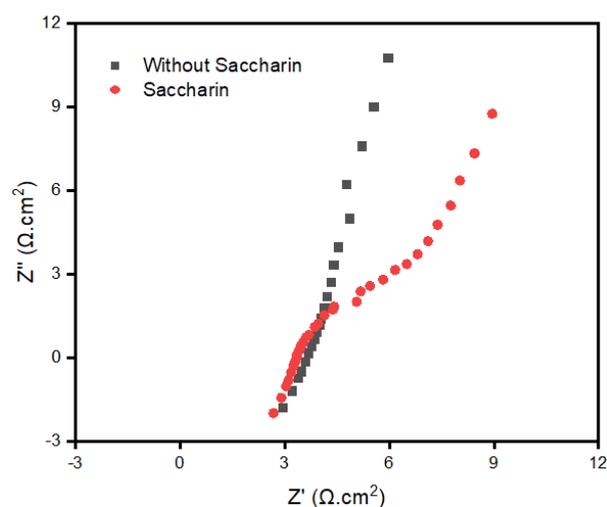


Figure 4. Nyquist Plot for SnNi with added saccharin and without saccharin.

The smallest values of R_{ct} shown in the samples with and without saccharin are 4.82 kHz and 15.77 kHz. The result of R_s in sample SnNi with and without saccharin are 3.44 Ω and 3.68 Ω . In these results, it was found that the

sample with saccharin has a smaller R_{ct} value. A high R_{ct} value indicates slow electron kinetics and high resistance to electrochemical reactions. In addition, the morphology of the sample also affects the impedance value produced because a more conductive or smoother surface can reduce the charge transfer resistance [32].

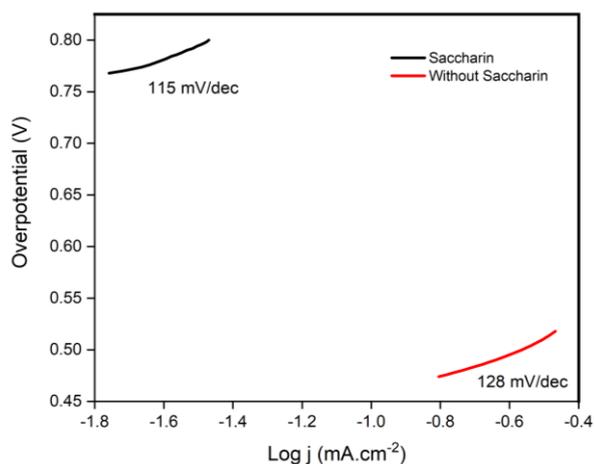


Figure 5. Tafel Slope of SnNi catalyst with and without the addition of saccharin.

LSV plots are used to study electron transfer reaction kinetics and parameters, such as overpotential, onset potential and catalyst tafel slope [33]. Tafel slope is a parameter commonly used to assess the rate and mechanism of electrocatalytic reactions. In simple terms, the Tafel slope states the number of mV needed to increase the current 10 times, with units of mV/dec [34]. Therefore, a low Tafel slope value is an indication of the presence of an active catalyst due to the excess potential required to achieve a higher current density is smaller [34]. The presence of overpotential in an electrocatalytic cell indicates that the cell requires more energy than predicted by thermodynamics to drive a reaction [33]. Based on the results shown in Fig. 5, the tafel slope value for the SnNi catalyst with the addition of saccharin is lower than that without the addition of saccharin, namely 115 mV/dec and 128 mV/dec respectively.

The activity and stability of SnNi catalysts without saccharin and with saccharin were also investigated by CA method conducted at constant potential at -0.20 V for 7200 s as shown in Fig. 6. The current-time transient presented in Fig. 6 shows that SnNi catalyst without saccharin has higher initial catalyst activity than SnNi with saccharin. The current density decreased quickly at first due to the accumulation of strong reaction intermediates adsorbed on the surface-active sites. Then, the current density decreased gradually and reached a pseudosteady state [22]. However, as the current density decreases, the

SnNi catalyst with saccharin has a slow decrease rate and higher stability than the SnNi catalyst without saccharin.

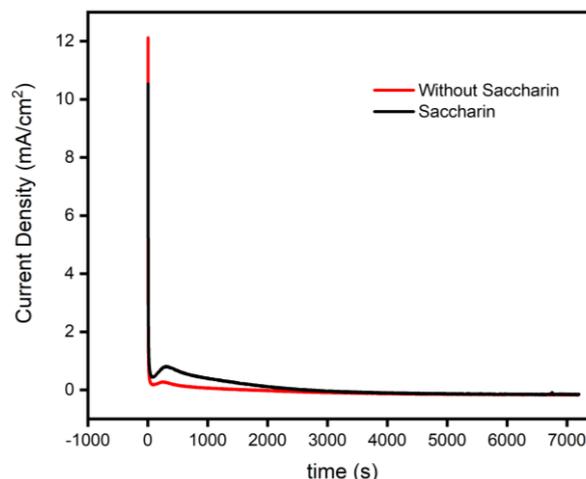


Figure 6. CA curves (relationship of current vs. time) for 7200 s of SnNi with added saccharin and without saccharin.

In CA curves, a slower decrease represents the catalyst's ability to maintain its activity and structure over time, which is the main characteristic of a stable catalyst. In addition, the presence of saccharin on the catalyst can influence the slower decrease in current density. Because it can act as a barrier or stabilizing agent on the surface of the catalyst, which helps protect the catalyst from contaminants or substances that can damage the structure of the resulting catalyst [35].

Figure 7 shows the CV measurement results of the SnNi electrocatalyst for the activity of the ethanol oxidation reaction. Conventional CV measurements are carried out with a three-electrode cell configuration, consisting of a working electrode, counter electrode and reference electrode. This technique measures the current response to a potential sweeping potential applied to a sample via a working electrode [36].

In Fig. 7a, the voltammogram of CV results for the SnNi catalyst without the addition of saccharin is presented which shows asymmetric peak results ($I_{pa}/I_{pc} \neq 1$) in the cathodic and anodic potentials. This indicates irreversibility in electron transfer [37]. Meanwhile, the CV test results for the SnNi catalyst with the addition of saccharin which can be seen in Fig. 7b show symmetric peaks of cathodic potential and anodic potential ($I_{pa}/I_{pc} = 1$). This indicates reversible electron transfer for this catalyst [38].

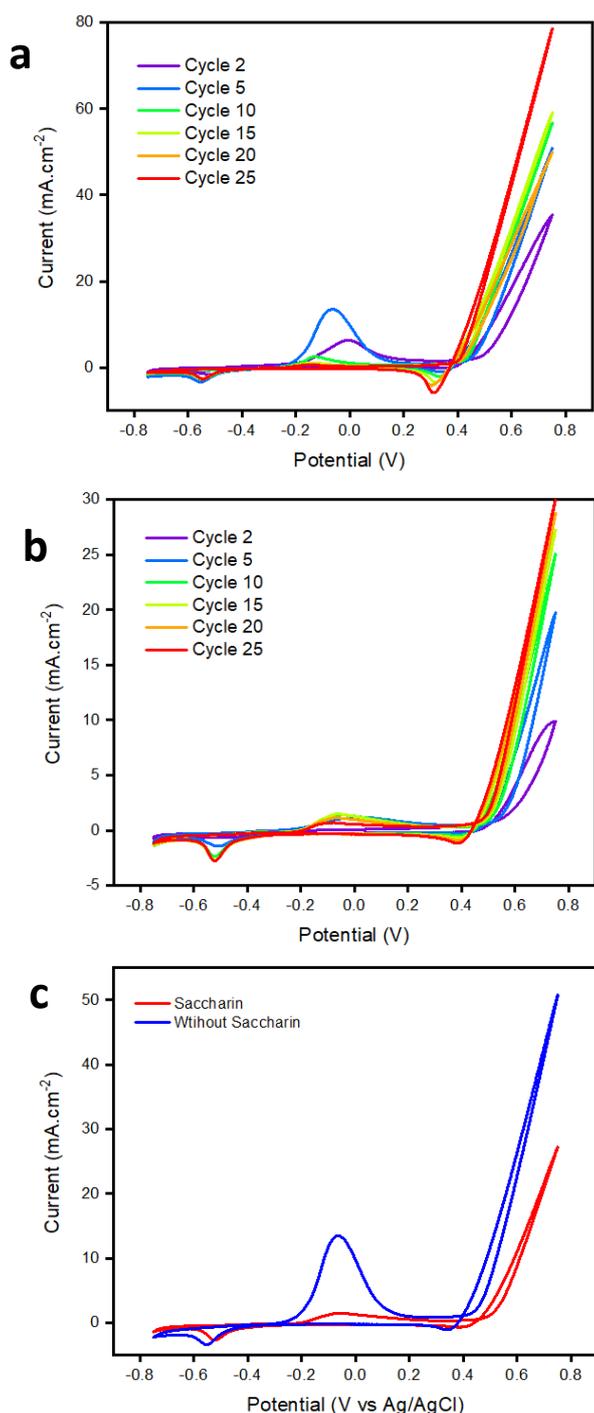


Figure 7. CV plots of SnNi electrocatalyst (a) without saccharin, (b) with saccharin for ethanol electrooxidation, (c) CV plots at the maximum peak of both the catalysts.

Electrochemically reversible reactions often result in rapid electron transfer between the species and the electrode, whereas electron transfer in irreversible reactions is slower [39]. The addition of saccharin to the SnNi catalyst acts as a smoothing agent and stress reliever which drastically affects the morphology, internal stress, hardness, microstructure and crystal structure of the

material being made and allows electrons to be electrochemically reversible [28,40].

This also shows that the SnNi catalyst with the addition of saccharin has the potential to increase the electron transfer rate at the electrode which will also increase its catalytic performance. Table 3 shows the j_f/j_b ratio that determined from the CV curves that show higher I_f/I_b ratio from SnNi catalyst with saccharin than without saccharin, suggesting a better catalytic tolerance to carbonaceous species for the SnNi catalyst with saccharin addition [41].

Table 3. Dependence of the backward scan peak current (j_b)/forward scan peak current (j_f) ratio determined from the CV curves

SnNi	j (mA.cm ⁻²)		j_f/j_b
	j_b	j_f	
without saccharin	2.63	1.02	0.38
with saccharin	1.78	0.98	0.55

4. Conclusion

SnNi alloy electrocatalyst were successfully synthesized through the electrodeposition method. The SnNi catalyst sample synthesized with the addition of saccharin showed better catalytic activity compared to the SnNi electrocatalyst without the addition of saccharin. Saccharin addition had a significant effect on the morphology, crystallite size, and composition of the catalyst. The presence of saccharin causes the formation of more uniform particles and has a smaller size. The sample with the addition of saccharin had a smaller R_{ct} value 4.82 Ω , lower tafel slope by 115 mV/dec, and show higher j_f/j_b ratio by 0.55. However, as the current density decreases, the SnNi catalyst with saccharin has a slow decrease rate and higher stability.

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References

- [1] M.A.F. Akhairi, S.K. Kamarudin, Catalysts in direct ethanol fuel cell (DEFC): An overview, *Int J Hydrogen Energy*. **41** (2016) 4214–4228. <https://doi.org/10.1016/j.ijhydene.2015.12.145>.
- [2] H. Burhan, M. Yılmaz, K. Cellat, A. Zeytun, G. Yılmaz, F. Şen, Direct ethanol fuel cells (DEFCs), in: *Direct Liquid Fuel Cells*, Elsevier, 2021: pp. 95–113.

- <https://doi.org/10.1016/B978-0-12-818624-4.00004-2>.
- [3] P. Bishnoi, K. Mishra, S.S. Siwal, V.K. Gupta, V.K. Thakur, Direct Ethanol Fuel Cell for Clean Electric Energy: Unravelling the Role of Electrode Materials for a Sustainable Future, *Advanced Energy and Sustainability Research*. **5** (2024). <https://doi.org/10.1002/aesr.202300266>.
- [4] J. Tayal, B. Rawat, S. Basu, Bi-metallic and tri-metallic Pt–Sn/C, Pt–Ir/C, Pt–Ir–Sn/C catalysts for electro-oxidation of ethanol in direct ethanol fuel cell, *Int J Hydrogen Energy*. **36** (2011) 14884–14897. <https://doi.org/10.1016/j.ijhydene.2011.03.035>.
- [5] B. Braunschweig, D. Hibbitts, M. Neurock, A. Wieckowski, Electrocatalysis: A direct alcohol fuel cell and surface science perspective, *Catal Today*. **202** (2013) 197–209. <https://doi.org/10.1016/j.cattod.2012.08.013>.
- [6] E. Berretti, L. Osmieri, V. Baglio, H.A. Miller, J. Filippi, F. Vizza, M. Santamaria, S. Specchia, C. Santoro, A. Lavacchi, Direct Alcohol Fuel Cells: A Comparative Review of Acidic and Alkaline Systems, *Electrochemical Energy Reviews*. **6** (2023) 30. <https://doi.org/10.1007/s41918-023-00189-3>.
- [7] D. Rohendi, A. Rachmat, N. Syarif, Fabrication and Characterization of Pt–Co/C Catalyst for Fuel Cell Electrode, *J Phys Conf Ser*. **1095** (2018) 012007. <https://doi.org/10.1088/17426596/1095/1/012007>.
- [8] W. Wang, X. Bai, X. Yuan, Y. Liu, L. Yang, F. Chang, Platinum–Cobalt Nanowires for Efficient Alcohol Oxidation Electrocatalysis, *Materials*. **16** (2023) 840. <https://doi.org/10.3390/ma16020840>.
- [9] Y. Zhu, L. Bu, Q. Shao, X. Huang, Subnanometer PtRh Nanowire with Alleviated Poisoning Effect and Enhanced C–C Bond Cleavage for Ethanol Oxidation Electrocatalysis, *ACS Catal*. **9** (2019) 6607–6612. <https://doi.org/10.1021/acscatal.9b01375>.
- [10] Z.A. Che Ramli, J. Pasupuleti, T.S. Tengku Saharuddin, Y.N. Yusoff, W.N.R.W. Isahak, L. Baharudin, C. Tak Yaw, S.P. Koh, S. Tiong Kiong, Electrocatalytic activities of platinum and palladium catalysts for enhancement of direct formic acid fuel cells: An updated progress, *Alexandria Engineering Journal*. **76** (2023) 701–733. <https://doi.org/10.1016/j.aej.2023.06.069>.
- [11] A.N. Golikand, M. Asgari, M.G. Maragheh, S. Shahrokhian, Methanol electrooxidation on a nickel electrode modified by nickel–dimethylglyoxime complex formed by electrochemical synthesis, *Journal of Electroanalytical Chemistry*. **588** (2006) 155–160. <https://doi.org/10.1016/j.jelechem.2005.11.033>.
- [12] X. Tan, S. Chen, D. Yan, R. Du, Q. Zhong, L. Liao, Z. Tang, F. Zeng, Recent advances in Ni-based catalysts for the electrochemical oxidation of ethanol, *Journal of Energy Chemistry*. **98** (2024) 588–614. <https://doi.org/10.1016/j.jechem.2024.06.045>.
- [13] Z. Angeles-Olvera, A. Crespo-Yapur, O. Rodríguez, J. Cholula-Díaz, L. Martínez, M. Videa, Nickel-Based Electrocatalysts for Water Electrolysis, *Energies (Basel)*. **15** (2022) 1609. <https://doi.org/10.3390/en15051609>.
- [14] A.N. Vyas, G.D. Saratale, S.D. Sartale, Recent developments in nickel based electrocatalysts for ethanol electrooxidation, *Int J Hydrogen Energy*. **45** (2020) 5928–5947. <https://doi.org/10.1016/j.ijhydene.2019.08.218>.
- [15] Y. Zhang, L. Zhang, C. Song, Y. Qin, L. Lu, W. Zhu, Z. Zhuang, Nickel chalcogenides as selective ethanol oxidation electro-catalysts and their structure–performance relationships, *Chemical Communications*. **58** (2022) 2496–2499. <https://doi.org/10.1039/D1CC07086J>.
- [16] Z. Miao, C. Xu, J. Zhan, Z. Xu, Morphology-control and template-free fabrication of bimetallic Cu–Ni alloy rods for ethanol electro-oxidation in alkaline media, *J Alloys Compd*. **855** (2021) 157438. <https://doi.org/10.1016/j.jallcom.2020.157438>.
- [17] M. Xia, T. Lei, N. Lv, N. Li, Synthesis and electrocatalytic hydrogen evolution performance of Ni–Mo–Cu alloy coating electrode, *Int J Hydrogen Energy*. **39** (2014) 4794–4802. <https://doi.org/10.1016/j.ijhydene.2014.01.091>.
- [18] G. Wang, W. Li, B. Huang, L. Xiao, J. Lu, L. Zhuang, Exploring the Composition–Activity Relation of Ni–Cu Binary Alloy Electrocatalysts for Hydrogen Oxidation Reaction in Alkaline Media, *ACS Appl Energy Mater*. **2** (2019) 3160–3165. <https://doi.org/10.1021/acsaem.8b02206>.
- [19] N.A.M. Barakat, M.T. Amen, F.S. Al-Mubaddel, M.R. Karim, M. Alrashed, NiSn nanoparticle-incorporated carbon nanofibers as efficient electrocatalysts for urea oxidation and working anodes in direct urea fuel cells, *J Adv Res*. **16** (2019) 43–53. <https://doi.org/10.1016/j.jare.2018.12.003>.
- [20] L.R. Vidales-Gallardo, E.N. Armendáriz-Mireles, G.G. Suarez-Velázquez, E. Rocha-Rangel, W.J. Pech-Rodríguez, Green and cost-effective synthesis of NiSn alloys by using intermittent microwave heating process as electrocatalysts for ethanol oxidation in

- alkaline solution, *J Mater Res.* **36** (2021) 4207–4215. <https://doi.org/10.1557/s43578-021-00271-w>.
- [21] M. Gao, X. Zhang, S. Dai, K.-W. Wang, Tin as a co-catalyst for electrocatalytic oxidation and reduction reactions, *Inorg Chem Front.* **11** (2024) 1019–1047. <https://doi.org/10.1039/D3QI02010J>.
- [22] J.D. Lović, S. Eraković Pantović, L.Z. Rakočević, N.L. Ignjatović, S.B. Dimitrijević, N.D. Nikolić, A Novel Two-Step Electrochemical Deposition Method for Sn-Pd Electrocatalyst Synthesis for a Potential Application in Direct Ethanol Fuel Cells, *Processes.* **11** (2023) 120. <https://doi.org/10.3390/pr11010120>.
- [23] J. Li, Z. Luo, Y. Zuo, J. Liu, T. Zhang, P. Tang, J. Arbiol, J. Llorca, A. Cabot, NiSn bimetallic nanoparticles as stable electrocatalysts for methanol oxidation reaction, *Appl Catal B.* **234** (2018) 10–18. <https://doi.org/10.1016/j.apcatb.2018.04.017>.
- [24] S. Budi, B. Kurniawan, D.M. Mott, S. Maenosono, A.A. Umar, A. Manaf, Comparative trial of saccharin-added electrolyte for improving the structure of an electrodeposited magnetic FeCoNi thin film, *Thin Solid Films.* **642** (2017) 51–57. <https://doi.org/10.1016/j.tsf.2017.09.017>.
- [25] S.H. Mosavat, M.E. Bahrololoom, M.H. Shariat, Electrodeposition of nanocrystalline Zn–Ni alloy from alkaline glycinate bath containing saccharin as additive, *Appl Surf Sci.* **257** (2011) 8311–8316. <https://doi.org/10.1016/j.apsusc.2011.03.017>.
- [26] S. Tebbakh, Y. Messaoudi, A. Azizi, N. Fenineche, G. Schmerber, A. Dinia, The influence of saccharin on the electrodeposition and properties of Co–Ni alloy thin films, *Transactions of the IMF.* **93** (2015) 196–204. <https://doi.org/10.1179/0020296715Z.00000000247>.
- [27] M. Taei, E. Havakeshian, H. Salavati, F. Abedi, Electrocatalytic oxidation of ethanol on a glassy carbon electrode modified with a gold nanoparticle-coated hydrolyzed CaFe–Cl layered double hydroxide in alkaline medium, *RSC Adv.* **6** (2016) 27293–27300. <https://doi.org/10.1039/C5RA20915C>.
- [28] H. Natter, R. Hempelmann, Nanocrystalline Copper by Pulsed Electrodeposition: The Effects of Organic Additives, Bath Temperature, and pH, *J Phys Chem.* **100** (1996) 19525–19532. <https://doi.org/10.1021/jp9617837>.
- [29] Y.R. Uhm, K.Y. Park, S.J. Choi, The effects of current density and saccharin addition on the grain size of electroplated nickel, *Research on Chemical Intermediates.* **41** (2015) 4141–4149. <https://doi.org/10.1007/s11164-013-1518-0>.
- [30] S. Hoghoghifard, H. Mokhtari, Improving the microwave absorption in Ni-coated fabrics by saccharin addition in plating bath, *Journal of Industrial Textiles.* **49** (2019) 402–411. <https://doi.org/10.1177/1528083718787525>.
- [31] L. Altamirano-Garcia, J. Vazquez-Arenas, M. Pritzker, R. Luna-Sánchez, R. Cabrera-Sierra, Effects of saccharin and anions (SO₄²⁻, Cl⁻) on the electrodeposition of Co–Ni alloys, *Journal of Solid State Electrochemistry.* **19** (2015) 423–433. <https://doi.org/10.1007/s10008-014-2616-7>.
- [32] Sh. Hassani, K. Raeissi, M.A. Golozar, Effects of saccharin on the electrodeposition of Ni–Co nanocrystalline coatings, *J Appl Electrochem.* **38** (2008) 689–694. <https://doi.org/10.1007/s10800-008-9488-4>.
- [33] N. Iqbal, S. Khan, F. Ahmad, Asian Journal of Nanoscience and Materials their Synthesis and Applications in Alcohol Fuel Cell, *Asian Journal of Nanoscience and Materials.* **3** (2023) 186–198. <https://doi.org/10.26655/AJNANOMAT.2023.3.2>.
- [34] O. van der Heijden, S. Park, R.E. Vos, J.J.J. Eggebeen, M.T.M. Koper, Tafel Slope Plot as a Tool to Analyze Electrocatalytic Reactions, *ACS Energy Lett.* **9** (2024) 1871–1879. <https://doi.org/10.1021/acsenergylett.4c00266>.
- [35] M. Xi, Z. Liu, J. Ding, W. Cheng, D. Jia, H. Lin, Saccharin Anion Acts as a “Traffic Assistant” of Zn²⁺ to Achieve a Long-Life and Dendritic-Free Zinc Plate Anode, *ACS Appl Mater Interfaces.* **13** (2021) 29631–29640. <https://doi.org/10.1021/acsaami.1c06307>.
- [36] H.-W. Wang, C. Bringans, A.J.R. Hickey, J.A. Windsor, P.A. Kilmartin, A.R.J. Phillips, Cyclic Voltammetry in Biological Samples: A Systematic Review of Methods and Techniques Applicable to Clinical Settings, *Signals.* **2** (2021) 138–158. <https://doi.org/10.3390/signals2010012>.
- [37] S. Baruah, A. Kumar, N.R. Peela, The promotional effect of Ag in activated carbon supported Pt-Ag nanoalloy electrocatalyst towards alkaline ethanol oxidation reaction: A kinetic study, *Journal of Electroanalytical Chemistry.* **953** (2024) 118015. <https://doi.org/10.1016/j.jelechem.2023.118015>.
- [38] M. Asadullah, S. Alva, A. Rinaldi, R. Sundari, CHLORIDE SENSOR FABRICATION BASED ON SPE Ag/AgCl THROUGH CYCLIC VOLTAMMETRIC TECHNIQUE: SCAN RATE EFFECT, *SINERGI.* **25** (2021) 351. <https://doi.org/10.22441/sinergi.2021.3.012>.

- [39] N. Elgrishi, K.J. Rountree, B.D. McCarthy, E.S. Rountree, T.T. Eisenhart, J.L. Dempsey, A Practical Beginner's Guide to Cyclic Voltammetry, *J Chem Educ.* **95** (2018) 197–206. <https://doi.org/10.1021/acs.jchemed.7b00361>.
- [40] Y.W. Li, X.X. Huang, J.H. Yao, X.S. Deng, Effect of Saccharin Addition on the Electrodeposition of Nickel from a Watts-Type Electrolyte, *Adv Mat Res.* **189–193** (2011) 911–914. <https://doi.org/10.4028/www.scientific.net/AMR.189-193.911>.
- [41] T.-H. Huang, D. Bhalothia, S. Lin, Y.-R. Huang, K.-W. Wang, The Ethanol Oxidation Reaction Performance of Carbon-Supported PtRuRh Nanorods, *Applied Sciences.* **10** (2020) 3923. <https://doi.org/10.3390/app10113923>.