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Effect of Pt–Ni/C Catalyst Composition Prepared via Impregnation–Ball Milling on Electrochemical Performance and Hydrogen Production in PEMWE

Novia Widia Ningsih[1], Dedi Rohendi[2,3]*, Addy Rachmat[2,3], Ady Mara[2], Muharni Muharni[2], Nyimas Febrika Sya'baniah[3,4], Dwi Hawa Yulianti[3,4], Diana Oktarina[1], Salsabilla Nabigha[1], and Yollanda Nurcholifah[5]

[1] Master Program, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, Palembang (Indonesia)
[2] Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, Palembang (Indonesia)
[3] Center of Research Excellent in Fuel Cell and Hydrogen, Universitas Sriwijaya, Palembang (Indonesia)
[4] Chemistry Program, Faculty of Computer and Science, Universitas Indo Global Mandiri, Palembang (Indonesia)
[5] Department of Chemistry, Faculty of Science and Engineering, Universitas Bangka Belitung, Balunijuk, Kepulauan Bangka Belitung, 33172, Indonesia

*Corresponding Author: rohendi19@unsri.ac.id

Abstract

This study investigates the effect of Pt–Ni/C catalyst composition prepared via impregnation and ball milling on electrochemical performance and hydrogen production in Proton Exchange Membrane Water Electrolysis (PEMWE). Five Pt:Ni ratios (1:0, 3:1, 1:1, 1:3, and 0:1) were evaluated using Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), and hydrogen production tests at 0.5–2.5 A. The Pt-rich catalyst (1:0) exhibited the highest intrinsic activity, with the largest charge (16.03×10^{-3} C) and electrochemically active surface area (4.90 m²/g), while the 3:1 composition showed the lowest charge transfer resistance. The 1:1 composition achieved the best hydrogen production performance at 2.9 mL/s under 1.5 A, with stable behavior across varying current conditions, indicating a synergistic Pt–Ni interaction that enhances catalytic efficiency. These findings establish a direct correlation between electrochemical characteristics and hydrogen production performance, demonstrating that optimal catalyst performance is governed by a balance between intrinsic activity, charge transfer properties, and active site availability. The Pt–Ni/C (1:1) catalyst represents a promising strategy for designing cost-effective electrocatalysts for PEMWE applications.

Keywords: Pt–Ni/C; impregnation; ball milling; PEMWE; hydrogen evolution reaction

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Abstrak (Indonesian)

Penelitian ini mengkaji pengaruh komposisi katalis Pt–Ni/C yang disintesis melalui kombinasi impregnasi dan *ball milling* terhadap kinerja elektrokimia dan produksi hidrogen pada sistem *Proton Exchange Membrane Water Electrolysis* (PEMWE). Lima rasio Pt:Ni (1:0, 3:1, 1:1, 1:3, dan 0:1) dievaluasi menggunakan *Linear Sweep Voltammetry* (LSV), *Cyclic Voltammetry* (CV), *Electrochemical Impedance Spectroscopy* (EIS), dan pengujian produksi hidrogen pada arus 0,5–2,5 A. Katalis kaya Pt (1:0) menunjukkan aktivitas intrinsik tertinggi dengan nilai muatan terbesar ($16{,}03 \times 10^{-3}$ C) dan luas permukaan aktif elektrokimia (ECSA) sebesar 4,90 m²/g, sedangkan komposisi 3:1 memiliki hambatan transfer muatan terendah. Komposisi 1:1 mencapai kinerja produksi hidrogen terbaik sebesar 2,9 mL/s pada arus 1,5 A dengan kestabilan yang baik pada berbagai kondisi arus, mengindikasikan interaksi sinergis Pt–Ni yang meningkatkan efisiensi katalitik. Temuan ini menetapkan korelasi langsung antara karakteristik elektrokimia dan kinerja produksi hidrogen, dan menunjukkan bahwa

kinerja katalis optimal ditentukan oleh keseimbangan antara aktivitas intrinsik, sifat transfer muatan, dan ketersediaan situs aktif. Katalis Pt–Ni/C (1:1) merupakan kandidat yang menjanjikan untuk pengembangan elektrokatalis yang hemat biaya pada aplikasi PEMWE.

Kata Kunci: Pt–Ni/C; impregnasi; ball milling; PEMWE; reaksi evolusi hidrogen

INTRODUCTION

The global energy crisis and environmental concerns associated with carbon emissions have accelerated the development of clean and renewable energy technologies, including the utilization of hydrogen as an alternative fuel [1]. Hydrogen possesses a high energy density and produces only water vapor as a by-product, and it can be sustainably generated through water electrolysis. This process involves the decomposition of water (H_2O) into hydrogen (H_2) and oxygen (O_2) using electrical energy, where hydrogen is produced at the cathode and oxygen at the anode [2].

Among various electrolysis technologies, Proton Exchange Membrane Water Electrolysis (PEMWE) has attracted significant attention due to its ability to produce high-purity hydrogen, high energy efficiency, and compact system design [3,4]. However, the performance of PEMWE is strongly influenced by the efficiency of electrocatalysts used to accelerate the hydrogen evolution reaction (HER) at the cathode.

Platinum (Pt) is widely regarded as one of the most effective catalysts for HER in acidic media; however, its high cost and limited availability hinder large-scale applications. To address this issue, bimetallic catalysts such as Pt–Ni have been extensively investigated due to their ability to enhance catalytic activity through synergistic effects and electronic structure modification [5]. The composition of Pt and Ni plays a crucial role in determining catalytic performance, as it affects the availability of active sites and the strength of metal–hydrogen interactions. An optimal Pt:Ni ratio can improve catalytic efficiency while reducing Pt usage, whereas excessive reduction of Pt content may lead to performance degradation [6,7].

To the best of our knowledge, studies that integrate synthesis strategy, catalyst composition, electrochemical behaviour, and hydrogen production performance within a single framework remain limited. This study uniquely integrates catalyst synthesis, electrochemical characterization (LSV, CV, and EIS), and direct hydrogen production evaluation within a single framework, enabling a comprehensive correlation between fundamental electrochemical properties and practical hydrogen generation performance.

Therefore, this study investigates the effect of Pt–Ni/C catalyst composition prepared via a combined impregnation–ball milling method on electrochemical performance and hydrogen production in PEMWE systems. In addition, a systematic correlation between electrochemical characteristics (LSV, CV, and EIS) and hydrogen production behaviour is established. The results provide a clear understanding of the trade-off between intrinsic catalytic activity and operational stability, offering practical insights into the rational design of Pt-efficient and cost-effective catalysts for PEM water electrolysis applications.

MATERIALS AND METHODS

Materials

The materials used in this study were Pt/C (40 wt%, Fuel Cell Store), $NiCl_2{\cdot}6H_2O$ (p.a., Merck), deionized water, ammonium hydroxide (NH_4OH, 3 M, p.a., Merck), hydrogen peroxide (H_2O_2, 3%, p.a., Merck), sulfuric acid (H_2SO_4, p.a., Merck), Vulcan XC-72R carbon (Fuel Cell Store), Avcarb P75T carbon paper (Fuel Cell Store), Nafion-117 membrane (Fuel Cell Store), ammonium bicarbonate (NH_4HCO_3), polytetrafluoroethylene (PTFE, Fuel Cell Store), isopropanol (2-propanol), and toluene (p.a., Merck) used as a process control agent (PCA).

Methods

Preparation of Pt–Ni/C catalyst via combined impregnation and ball milling

Vulcan XC-72R carbon in **Table 1** was dispersed in 25 mL of deionized water and homogenized using an ultrasonic homogenizer for 30 min. Subsequently, $NiCl_2{\cdot}6H_2O$ was added and stirred until completely mixed. Ammonium hydroxide (NH_4OH) was then added dropwise until the solution reached pH 10, followed by continuous stirring for 24 h. The mixture was dried at 110 °C for 3 h and calcined at 450 °C for 5 h. Reduction was performed under hydrogen gas flow for 3 h at 350 °C to obtain the Ni/C catalyst.

The synthesized Ni/C catalyst was then mixed with Pt/C as in **Table 1** and toluene as a process control agent (PCA). The mixture was subjected to ball milling with a ball-to-powder ratio (BPR) of 10:1 for 1 h. The resulting powder was dried at 115 °C for 1 h to obtain the Pt–Ni/C catalyst.

Table 1. Calculation of Pt–Ni/C component content

No.	Composition Ratio		Mass (gram)		
	Pt	Ni	Pt/C (40% Pt on C)	Carbon Vulcan XC-72R	$NiCl_2.6H_2O$
1.	1	0	0.0625	0	0
2.	1	3	0.0156	0.0374	0.0623
3.	1	1	0.0313	0.0249	0.0415
4.	3	1	0.0469	0.0207	0.0207
5.	0	1	0	0.0499	0.083

Fabrication of Electrodes

Pt–Ni/C catalysts with Pt:Ni ratios of 1:0, 3:1, 1:1, 1:3, and 0:1 was used for electrode fabrication. The catalyst powder was first dispersed in deionized water and stirred thoroughly. Isopropanol was then added, followed by ultrasonication for 10 min. Nafion and PTFE were subsequently added, and the mixture was further ultrasonicated for 5 min to obtain a homogeneous catalyst ink.

The catalyst ink was loaded into a spray gun and deposited onto a gas diffusion layer (GDL). The coating was applied in three successive layers. The first layer consisted of Pt–Ni/C catalyst, isopropanol, and PTFE, followed by sintering at 350 °C for 3 h. The second layer consisted of Pt–Ni/C catalyst, isopropanol, and Nafion, while the third layer consisted of isopropanol and Nafion. The resulting electrodes had dimensions of 5 cm × 5 cm.

Fabrication of membrane electrode assembly (MEA)

The membrane electrode assembly (MEA) was prepared by hot-pressing the cathode and anode onto both sides of a Nafion-117 membrane. Prior to assembly, the membrane was pretreated by immersion in 3% H_2O_2 solution at 80 °C for 1 h to remove organic contaminants, followed by rinsing with deionized water. The membrane was then immersed in 0.5 M H_2SO_4 at 80 °C for 1 h and thoroughly washed with deionized water.

The prepared electrodes were placed on both sides of the membrane, sandwiched between aluminum foil sheets, and pressed between aluminum plates. The assembly was hot-pressed at 135 °C and 2000 psi for 3 min to obtain the MEA.

Hydrogen production test

The fabricated MEAs were tested for hydrogen production using a laboratory-scale electrolyzer connected to a power supply. The system was operated at applied currents of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 A for each catalyst composition (1:0, 3:1, 1:1, 1:3, and 0:1), with each experiment conducted in triplicate.

The outlet gas was directed into a 250 mL graduated cylinder filled with water to measure hydrogen production via water displacement. The time required for a fixed volume displacement (250 mL) was recorded to determine the hydrogen production rate. A schematic diagram of the electrolyzer system is presented in **Figure 1**.

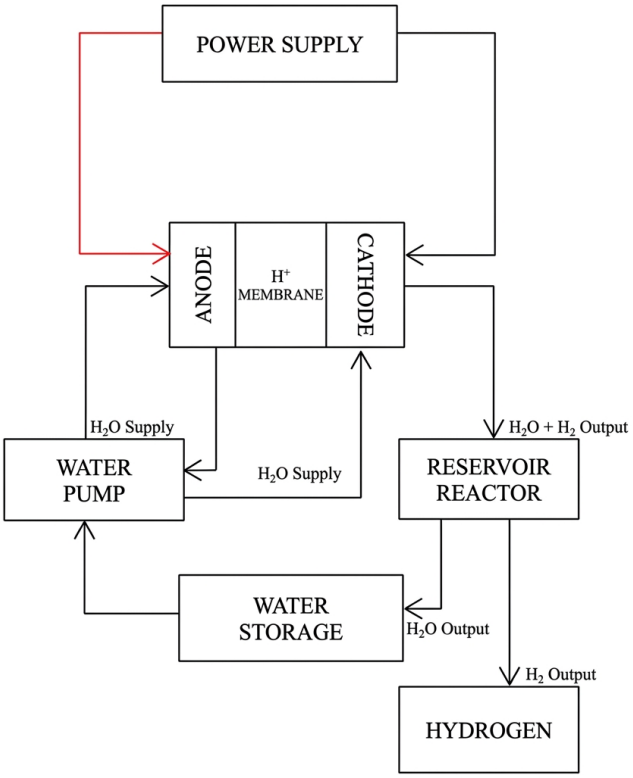

Figure 1. Schematic Diagram of the Electrolyzer.

RESULTS AND DISCUSSION

Synthesis of Pt–Ni/C catalysts

Platinum-based catalysts modified with transition metals such as Ni have been widely reported to enhance catalytic performance for the Hydrogen Evolution Reaction (HER), while simultaneously reducing the required amount of Pt without compromising overall system efficiency [8,9]. Therefore, Pt–Ni/C catalysts were synthesized in this study.

The synthesis of Ni-based catalysts is commonly carried out through the reduction of nickel salt precursors, such as nickel(II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$). In this work, the formation of Ni species proceeded via a precipitation–calcination–reduction route, as described below:

Formation of metal hydroxide:

$$NiCl_2 \cdot 6H_2O + 2NH_4OH \rightarrow Ni(OH)_2\downarrow + 2NH_4Cl + 6H_2O \quad (1)$$

Calcination process:

$$Ni(OH)_2 \rightarrow NiO + H_2O \quad (2)$$

Reduction process:

$NiO + H_2 \rightarrow Ni + H_2O$ .....(3)

The Pt/C used in this study was a commercial catalyst containing 40 wt% Pt dispersed on carbon. The synthesis of Pt–Ni/C catalysts was carried out by impregnating Ni species onto the Pt/C support, which can be generally represented as:

Pt/C (40 wt%) + Ni → Pt–Ni/C .....(4)

The incorporation of Ni into Pt is expected to modify the electronic structure of Pt and optimize the binding strength of hydrogen intermediates, thereby enhancing catalytic activity toward HER while reducing Pt usage. This synergistic interaction between Pt and Ni plays a key role in improving catalytic performance in PEMWE systems [5].

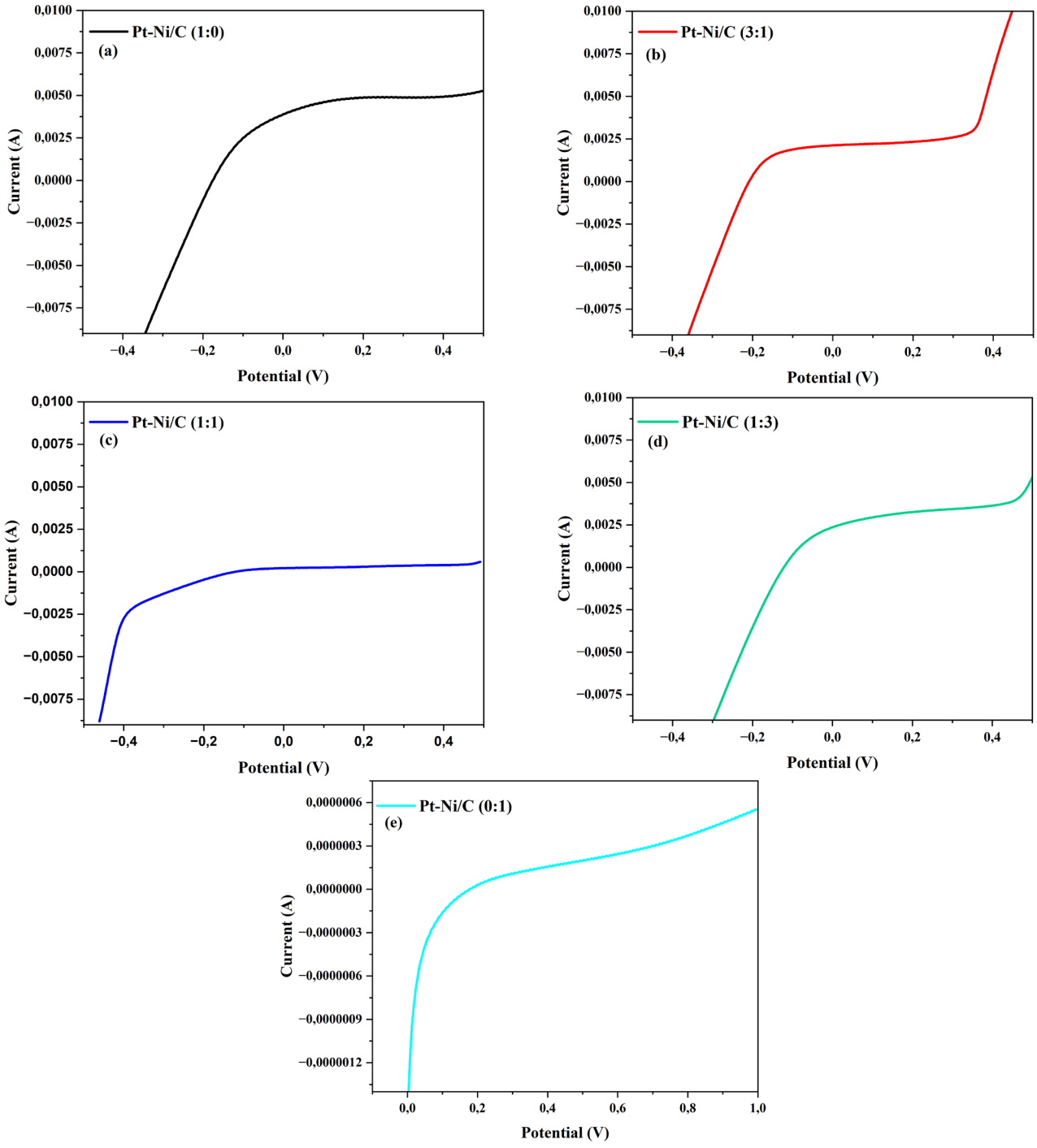

Figure 2. LSV curves of Pt–Ni/C electrodes with different compositions (a) 1:0, (b) 3:1, (c) 1:1, (d) 1:3, and (e) 0:1.

Linear sweep voltammetry (LSV) analysis

Linear Sweep Voltammetry (LSV) analysis was conducted to evaluate the electrocatalytic activity of Pt–Ni/C electrodes toward the Hydrogen Evolution Reaction (HER) at various Pt:Ni compositions. This technique provides insight into the relationship between applied potential and current density, which reflects reaction kinetics and catalytic activity in PEMWE systems [10]. Furthermore, LSV analysis also plays an important role in determining the electrochemical potential window, ensuring system stability and feasibility for electrolysis applications, particularly with regard to the maximum tolerable voltage limit before electrolyte decomposition occurs [11]. The LSV curves presented in **Figure 2** illustrate the current response as a function of potential for each catalyst composition.

The LSV results show that the 1:0 composition in **Figure 2 (a)** exhibits the highest current density, followed by the 1:3 in **Figure 2 (d)** and 3:1 in **Figure 2 (b)** compositions, while the 1:1 composition in **Figure 2 (c)** shows a relatively lower current density. The 0:1 composition in **Figure 2 (e)** demonstrates the lowest activity. This trend indicates that the Pt–Ni/C ratio plays a critical role in governing electrocatalytic performance toward HER.

The quantitative data in **Table 2** further support these observations. The 1:0 composition exhibits the highest charge (Q) value of 16.03×10^{-3} C, followed by 1:3 (13.11×10^{-3} C) and 3:1 (12.10×10^{-3} C), while the 1:1 composition shows a significantly lower value of 4.50×10^{-3} C. The lowest Q value is observed for the 0:1 composition (2.31×10^{-6} C). These results suggest that Pt content strongly influences the availability of active sites and charge transfer during HER, whereas pure Ni exhibits limited catalytic activity in acidic environments.

Table 2. LSV analysis results of Pt–Ni/C electrodes prepared via impregnation–ball milling

No.	Pt–Ni/C Ratio	Q (C)
1.	1:0	16.03×10^{-3}
2.	3:1	12.10×10^{-3}
3.	1:1	4.50×10^{-3}
4.	1:3	13.11×10^{-3}
5.	0:1	2.31×10^{-6}

The non-linear relationship between Pt–Ni composition and HER activity suggests that catalytic performance is influenced not only by composition ratio but also by electronic interactions and surface structure. Previous studies have shown that alloying Pt with Ni can modify the adsorption energies of key intermediates such as H and OH, thereby affecting reaction pathways and catalytic activity [12].

Overall, these findings confirm that Pt remains the dominant factor in enhancing HER activity, while the addition of Ni at specific ratios, such as 1:3, can provide synergistic effects through electronic interaction and surface modification, thereby facilitating hydrogen formation and improving catalytic performance [13].

Cyclic voltammetry (CV) analysis

Cyclic Voltammetry (CV) analysis is an electrochemical technique based on the principle of potential sweeping, in which the current response is measured as a function of an applied potential that varies linearly with time [11]. This method produces voltammograms that represent oxidation–reduction processes occurring at the electrode surface. The data obtained from the voltammograms are further used to calculate the Electrochemically Active Surface Area (ECSA) [14].

In this study, the ECSA was calculated using Equation (5):

$$\text{ECSA} = \frac{Q_H}{Q_C \times m} \quad \text{.....(5)}$$

Where:

ECSA : Electrochemically Active Surface Area (m^2/g)
Q_H : average charge per unit electrode area (C)
Q_C : charge required to oxidize a monolayer of catalyst ($\mu C \cdot cm^{-2}$)
m : catalyst mass (g) [15].

CV characterization was conducted to evaluate the electrochemical response and determine the electrochemically active surface area (ECSA) of Pt–Ni/C electrodes at various Pt:Ni compositions (1:0, 3:1, 1:1, 1:3, and 0:1). The voltammograms for each composition are presented in **Figure 3**, while the calculated ECSA values are summarized in **Table 3**.

Based on **Figure 3**, the 1:0 composition exhibits the highest current response, followed by the 1:1 composition, while the 3:1 and 1:3 composition show relatively lower responses. The pure Ni composition exhibits very low current. This trend indicates that Pt plays a dominant role in surface redox processes, whereas Ni primarily contributes through indirect electronic and structural modification of the catalyst surface.

Table 3 shows that the 1:0 composition has the highest ECSA value of 4.90 m^2/g, followed by 1:1 with 2.51 m^2/g. The 1:3 and 3:1 composition exhibit ECSA values of 1.59 m^2/g and 1.49 m^2/g, respectively, while pure Ni shows a significantly lower value of 6.88×10^{-4} m^2/g. These results suggest that the availability of

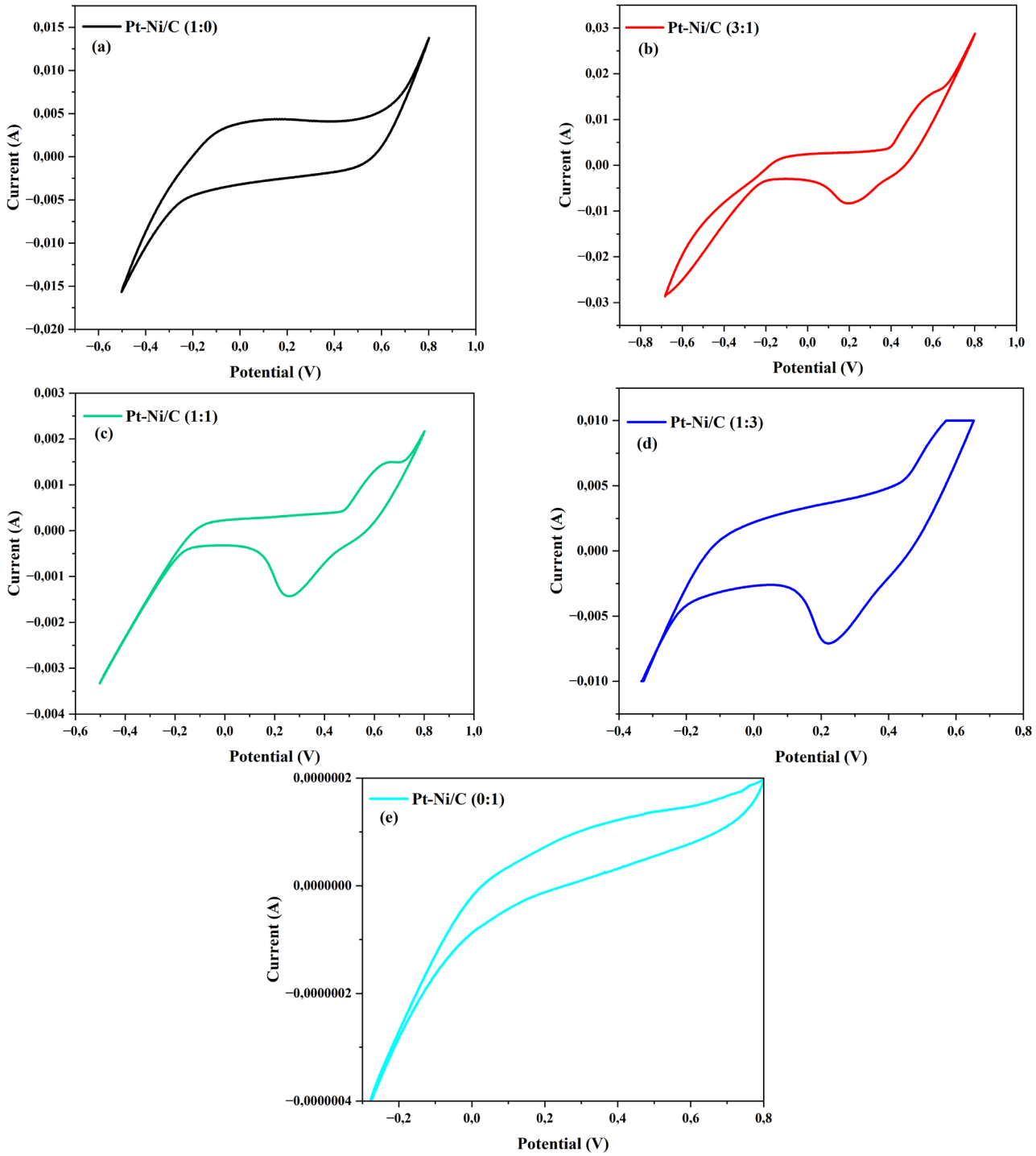

Figure 3. Voltammograms of Pt–Ni/C electrodes with different compositions (a) 1:0, (b) 3:1, (c) 1:1, (d) 1:3, and (e) 0:1.

electrochemically active sites are maximized in Pt-rich compositions, while Ni incorporation influences surface characteristics without directly contributing a significant number of active sites. This observation is consistent with previous studies reporting that Pt serves as the primary active center, while Ni acts as a promoter enhancing surface interactions at specific compositions [16].

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surface characteristics without directly contributing a significant number of active sites. This observation is consistent with previous studies reporting that Pt serves as the primary active center, while Ni acts as a promoter enhancing surface interactions at specific compositions [16].

Table 3. ECSA values of Pt–Ni/C electrodes prepared via impregnation–ball milling

No.	Pt–Ni/C Ratio	ECSA (m^2/g)
1.	1:0	4.90
2.	3:1	1.49
3.	1:1	2.51
4.	1:3	1.59
5.	0:1	6.88×10^{-4}

Interestingly, although the 1:1 composition exhibits a higher ECSA than the 1:3 and 3:1 compositions, its charge (Q) value obtained from LSV is lower. This discrepancy implies that a higher density of active sites does not necessarily correspond to higher intrinsic catalytic activity per site. This behavior can be attributed to electronic interactions between Pt and Ni, which may shift the Pt d-band center and alter the hydrogen adsorption energy (H*), leading to non-optimal adsorption–desorption behavior for HER [17].

In addition, the alloy structure at the 1:1 ratio may be less favourable for efficient charge transfer, thereby reducing the overall charge contribution observed in LSV. This suggests that both electronic effects and charge transfer limitations contribute to the reduced intrinsic activity observed at this composition.

Therefore, although the 1:1 composition exhibits a relatively high density of active sites, the kinetic effectiveness per site is lower compared to compositions richer in either Pt or Ni. This finding indicates that catalytic performance is governed not only by the number of active sites but also by their intrinsic activity and electronic environment.

Overall, the CV and ECSA results confirm that Pt is the dominant component governing electrocatalytic activity, while the addition of Ni at specific ratios provides synergistic effects, particularly in improving material utilization and reducing Pt loading without significantly compromising catalytic performance.

Electrochemical impedance spectroscopy (EIS) analysis

Electrochemical Impedance Spectroscopy (EIS) is an electroanalytical technique used to investigate material properties and electrochemical reactions by analyzing the electrical impedance of a system. This non-destructive *in situ* technique has been widely applied in various fields, including fuel cells, corrosion studies, batteries, and electrocatalysis, for performance evaluation and diagnostic analysis of electrochemical systems [18].

In this study, EIS characterization was conducted to evaluate the series resistance (Rs), polarization resistance (Rp), and conductivity behavior of Pt–Ni/C electrodes with different Pt:Ni compositions. The Nyquist plots shown in **Figure 4** illustrate the variation in semicircle diameter, which corresponds to differences in polarization resistance (Rp) for each composition. The electrical conductivity (σ) was calculated using Equation (6):

$$\sigma = \frac{l}{R \times A} \quad \text{.....(6)}$$

where:

σ = conductivity (S/cm)
l = sample thickness (cm)
R = total resistance (Ω), where R = (Rs+Rp)
A = electrode contact area (cm^2) [19].

For the 1:0 in **Figure 4 (a)** and 3:1 in **Figure 4 (b)** compositions, relatively small semicircle diameters are observed, indicating low polarization resistance (Rp) and efficient charge transfer processes [20,21]. In contrast, the 1:1 composition in **Figure 4 (c)** exhibits a significantly larger semicircle diameter, suggesting increased polarization resistance. The 1:3 composition in **Figure 4 (d)** shows a reduced semicircle diameter compared to 1:1, indicating improved charge transfer pathways. Meanwhile, the pure Ni electrode 0:1 in **Figure 4 (e)** displays a very large semicircle diameter with impedance in the kilo-ohm range, indicating dominant electrochemical resistance and very low electrical conductivity. This trend indicates that catalyst composition strongly governs charge transfer kinetics and interfacial resistance.

The quantitative data in **Table 4** further confirm these observations. The 1:0 composition exhibits Rp = 15 Ω, Rs = 9 Ω, and total resistance of 24 Ω, with a conductivity of 41.67×10^{-3} S/cm. The 3:1 composition shows lower Rs (6.78 Ω) and total resistance (21.78 Ω), yielding a higher conductivity of 45.91×10^{-3} S/cm, indicating that higher Pt content enhances electron transport efficiency. Notably, ECSA reflects the charge storage capacity of the electrical double layer, while impedance is more sensitive to electron conduction pathways and electrode pore characteristics [22], which accounts for the observed discrepancy between the two parameters across different compositions.

In contrast, the 1:1 composition shows a significant increase in both Rp (31.5 Ω) and Rs (72.1

Ω), resulting in the highest total resistance (103.6 Ω) among the Pt–Ni compositions and a decrease in conductivity to 9.65 × 10^{-3} S/cm. This indicates that both polarization and ohmic resistances become dominant at this composition, limiting electron transport efficiency.

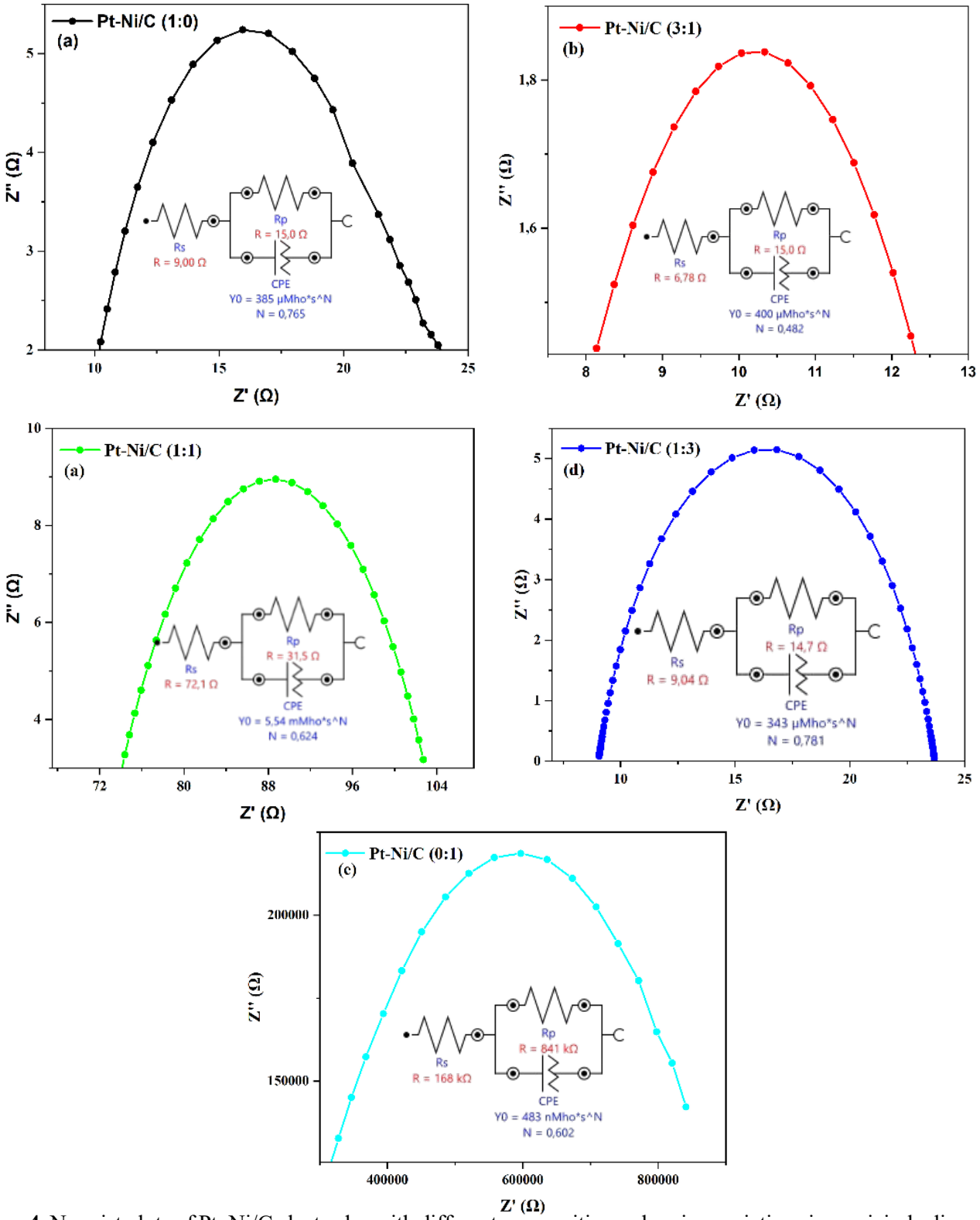

Figure 4. Nyquist plots of Pt–Ni/C electrodes with different compositions, showing variations in semicircle diameter corresponding to polarization resistance (Rp).

Table 4. Impedance parameters and conductivity of Pt–Ni/C electrodes prepared via impregnation–ball milling

No.	Pt–Ni/C	Impedance Parameter			Conductivity (S/cm)
		Rp(Ω)	Rs(Ω)	R(Ω)	
1.	1:0	15	9	24	41.67×10^{-3}
2.	3:1	15	6.78	21.78	45.91×10^{-3}
3	1:1	31.5	72.1	103.6	9.65×10^{-3}
4.	1:3	14.7	9.04	24.3	42.12×10^{-3}
5.	0:1	841×10^{3}	168×10^{3}	1.009×10^{3}	9.9×10^{-8}

For the 1:3 composition, Rp and Rs values of 14.7 Ω and 9.04 Ω, respectively, result in a total resistance of 24.3 Ω, with conductivity increasing again to 42.12×10^{-3} S/cm. In contrast, the pure Ni electrode (0:1) exhibits extremely high Rp (841×10^{3} Ω) and Rs (168×10^{3} Ω), leading to very low conductivity. This behavior confirms that Ni alone exhibits poor electrochemical performance in acidic environments due to its high resistance and limited charge transfer capability [6].

The combined interpretation of the EIS and LSV results indicates that the 3:1 and 1:3 compositions, which exhibit lower Rp values and higher conductivity, also produce relatively higher current densities. This suggests that lower charge transfer resistance is correlated with improved electrochemical reaction kinetics and enhanced HER activity at higher overpotentials [23]. Recent studies have also shown that an integrated evaluation using EIS, LSV, and ECSA provides a more comprehensive understanding of catalyst performance [24].

However, the CV results reveal that the ECSA values for these compositions are relatively lower, indicating a limited number of available electrochemically active sites. Considering that ECSA represents the active surface area accessible for the reaction, lower values may limit the overall catalytic activity, despite the relatively efficient charge transfer process [25]. This observation suggests a trade-off between conductivity and the availability of active sites in determining the overall catalytic performance [26].

Conversely, this result indicates that the 1:1 composition provides a higher density of electrochemically active sites, which may compensate for its relatively lower electron transport efficiency [27]. This behavior can be attributed to the crucial role of active surface sites in determining catalytic activity, where a higher availability of active sites can significantly enhance the overall reaction rate [28]. Furthermore, impedance parameters such as polarization resistance (Rp) do not solely dictate catalytic activity, as EIS-derived parameters reflect overall system response and do not directly account for the number or accessibility of active sites [22]. This suggests that catalytic performance is governed by the balance between conductivity (electron transport) and active site availability, both of which originate from catalyst structure and morphology [6].

This phenomenon can be attributed to the intrinsic characteristics of Pt–Ni alloys, which exhibit lattice strain and electronic structure modifications that do not vary linearly with composition. At the balanced ratio (1:1), lattice distortion and surface configuration may favor the formation of abundant active sites, even though electron transport is less efficient. This behavior is consistent with the concept of electronic–geometric nonlinearity, where structural and electronic properties do not scale proportionally with composition [29].

Overall, the EIS results demonstrate that low electrochemical resistance does not always directly correlate with high surface activity unless accompanied by sufficient ECSA. This finding suggests that optimal catalytic performance arises from a balance between polarization resistance, active site availability, and electron transport efficiency. The integration of EIS, CV, and LSV results further confirms that the 1:1 composition, despite having higher Rp and Rs values, provides enhanced surface activity due to a greater density of active sites. Therefore, EIS interpretation should be combined with surface-related parameters to achieve a comprehensive understanding of the electrochemical behavior of Pt–Ni/C catalysts.

Hydrogen production

Global hydrogen production is still predominantly based on fossil fuel processes, particularly steam methane reforming (SMR), which generates significant CO_2 emissions [30]. This has driven the development of more sustainable hydrogen production technologies, one of which is water electrolysis, which is considered environmentally friendly due to its zero carbon emissions [3].

Among various electrolysis technologies, Proton Exchange Membrane (PEM) systems have attracted considerable attention due to their ability to produce

high-purity hydrogen, with oxygen as a by-product, making them a promising clean energy source [3,4].

In PEM systems operating under acidic conditions, the Hydrogen Evolution Reaction (HER) proceeds through two primary mechanisms, namely the Volmer–Heyrovsky and Volmer–Tafel pathways **Figures 5** and **6**, which govern the kinetics of hydrogen formation at the electrode surface [5]. The Volmer step **Equation 7** produces adsorbed hydrogen (H*), which subsequently reacts via either the Heyrovsky step **Equation 8** or the Tafel step **Equation 9** to form molecular hydrogen (H_2). The efficiency of HER is strongly influenced by hydrogen adsorption energy, the number of active sites, and charge transfer capability at the catalyst surface.

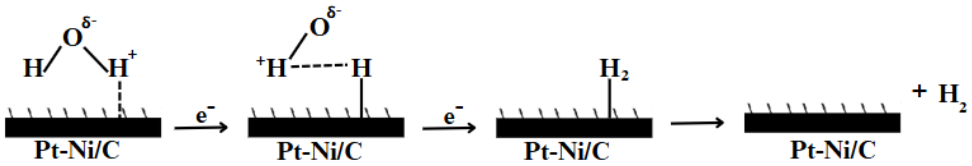

Figure 5. Hydrogen reaction mechanism via the Volmer–Heyrovsky pathway

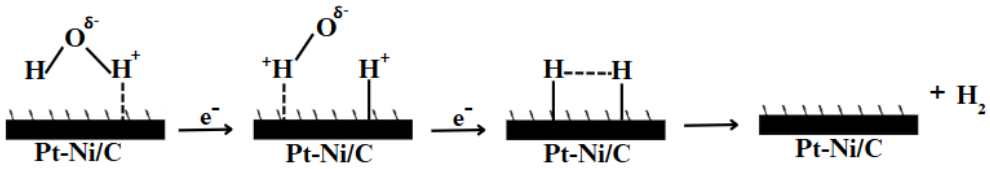

Figure 6. Hydrogen reaction mechanism via the Volmer–Tafel pathway

$H^+ + e^- = H_{ad}$ .....(7)

$H^+ + e^- + H_{ad} = H_2$ .....(8)

$2H_{ad} = H_2$ .....(9)

The performance of Pt–Ni/C catalysts in hydrogen production was evaluated by measuring the hydrogen production rate at different Pt–Ni/C compositions and operating currents (0.5–2.5 A). The hydrogen production rate was calculated using Equation (10):

$$QH_2 = \frac{\Delta V}{\Delta t} \quad \text{..... (10)}$$

where:

QH_2 : hydrogen production rate (mL/s)

ΔV : volume of hydrogen produced (mL)

Δt : time (s)

The experimental results are presented in **Figure 7**.

The results show that the hydrogen production rate does not increase monotonically with increasing current, but instead reaches a maximum at a specific current before declining or plateauing. At 0.5 A, the hydrogen production rate is relatively low for all catalyst compositions. As the current increases to 1.0 A, the production rate rises and reaches its highest value for the Pt–Ni/C (1:1) composition.

The maximum hydrogen production rate is observed at 1.5 A, where the Pt–Ni/C (1:0) composition exhibits the highest absolute value, closely followed by the Pt–Ni/C (1:1) composition. However, at higher currents (2.0–2.5 A), the hydrogen production rate decreases for most compositions. This behavior suggests that the hydrogen evolution reaction is increasingly controlled by kinetic factors at higher current densities, where limitations associated with the rate-determining steps hinder further improvement in reaction efficiency [31].

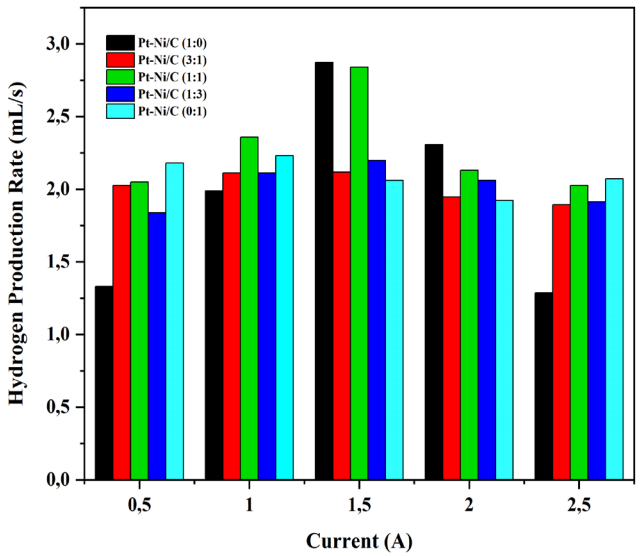

Figure 7. Hydrogen production rate of Pt–Ni/C catalysts at various compositions as a function of applied current (0.5–2.5 A).

Although Pt–Ni/C (1:0) exhibits the highest peak hydrogen production rate under certain conditions, its performance is not consistent across the entire current range. In contrast, the Pt–Ni/C (1:1) composition demonstrates relatively stable performance with consistently high hydrogen production rates under varying operating conditions. This indicates that the 1:1 composition provides enhanced stability under operating conditions and improved durability, which may contribute to more effective utilization of Pt [32].

This behavior can be further explained by the electronic structure modulation of Pt induced by Ni incorporation. According to the d-band center theory, the addition of transition metals shifts the d-band center of Pt, thereby tuning the hydrogen adsorption free energy (ΔG_H) [33]. An optimal HER catalyst should exhibit a ΔG_H value close to zero, ensuring a balanced hydrogen adsorption–desorption process.

This suggests that the Pt–Ni (1:1) composition may provide near-optimal hydrogen binding strength due to electronic interactions between Pt and Ni, leading to improved catalytic efficiency and operational stability. In contrast, deviations from the optimal hydrogen binding strength can limit HER performance, where excessively strong binding hinders hydrogen desorption, while overly weak binding reduces hydrogen adsorption, both leading to decreased catalytic activity [34].

The 3:1 (Pt-rich) and 1:3 (Ni-rich) compositions exhibit moderate performance. In the 3:1 composition, the contribution of Ni to electronic modification is limited, while in the 1:3 composition, the higher Ni content may reduce catalyst stability in acidic media due to partial Ni dissolution and increased interfacial resistance. Meanwhile, the pure Ni electrode (0:1) shows the lowest hydrogen production rate across all current ranges. This indicates that the absence of Pt results in non-optimal hydrogen adsorption energy and poor charge transfer capability, thereby limiting HER activity [7].

Overall, the results indicate that while Pt–Ni/C (1:0) provides the highest peak performance under specific conditions, the Pt–Ni/C (1:1) composition offers the best balance between performance stability and Pt utilization efficiency. Therefore, the 1:1 composition represents a promising candidate for the development of cost-effective and sustainable catalysts for PEM water electrolysis applications.

The overall electrochemical performance of Pt–Ni/C catalysts is governed by the interplay between intrinsic catalytic activity, electrochemically active surface area, and charge transfer properties. LSV results indicate that Pt-rich compositions exhibit higher intrinsic catalytic activity, while EIS analysis demonstrates that the 3:1 and 1:3 compositions possess lower charge transfer resistance and improved conductivity. However, CV analysis reveals that the 1:1 composition provides a relatively higher electrochemically active surface area, indicating a greater density of active sites. This suggests that optimal hydrogen production is achieved not by maximizing a single parameter, but by balancing activity, surface availability, and electron transport.

These findings suggest that optimal hydrogen evolution performance is not determined by a single parameter, but rather by a synergistic balance between active site availability, electron transport efficiency, and hydrogen adsorption characteristics (ΔG_H*). This explains why the 1:1 composition demonstrates superior stability and overall hydrogen production performance, despite not exhibiting the highest intrinsic activity or the lowest resistance individually.

Despite these promising results, this study is limited to short-term electrochemical evaluation under controlled laboratory conditions. Further investigation on long-term stability and durability is required to fully validate the practical applicability of the Pt–Ni/C catalysts in PEM water electrolysis systems.

CONCLUSION

This study demonstrates that the composition of Pt–Ni/C catalysts play a crucial role in determining electrochemical behaviour and hydrogen production performance in Proton Exchange Membrane Water Electrolysis (PEMWE) systems. Catalysts synthesized via the combined impregnation–ball milling method exhibit distinct properties depending on the Pt:Ni ratio, highlighting the importance of composition in tuning catalytic characteristics.

Electrochemical analysis reveals that Pt-rich compositions exhibit superior intrinsic activity, as indicated by higher current response and electrochemically active surface area (ECSA), while compositions with moderate Ni content demonstrate improved charge transfer properties and electrical conductivity. However, these advantages do not necessarily translate into optimal hydrogen production performance, indicating that catalytic efficiency is governed by multiple interrelated factors rather than a single parameter.

Importantly, this study establishes a direct correlation between electrochemical characteristics (LSV, CV, and EIS) and actual hydrogen production behaviour. The results demonstrate a non-linear relationship between catalyst composition and performance, where the balanced Pt–Ni/C (1:1)

composition achieves the most stable and efficient hydrogen production across varying operating conditions. This finding highlights the trade-off between intrinsic catalytic activity, charge transfer efficiency, and active site availability.

Therefore, the Pt–Ni/C (1:1) catalyst provides the most favourable balance between performance stability and Pt utilization efficiency, demonstrating the feasibility of reducing noble metal content without significantly compromising catalytic performance.

Overall, this work provides valuable insights into the rational design of cost-effective and Pt-efficient electrocatalysts for PEM water electrolysis applications. These findings offer a practical strategy for optimizing catalyst composition through the synergistic control of electronic structure, surface properties, and charge transport behavior, thereby contributing to the advancement of sustainable hydrogen production technologies. This integrated approach provides a more comprehensive understanding compared to conventional studies that focus on individual electrochemical parameters.

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