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Electrochemical investigation of novel reference electrode Ni/Ni(OH)$_2$ in comparison with silver and platinum inert quasi-reference electrodes for electrolysis in eutectic molten hydroxide

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Abstract

An efficient and green energy carrier hydrogen (H_2) generation via water splitting reaction has become a major area of focus to meet the demand of clean and sustainable energy sources. In this research, the splitting steam via eutectic molten hydroxide (NaOH-KOH; 49–51 mol%) electrolysis for hydrogen gas production has been electrochemically investigated at 250–300 ^oC. Three types of reference electrodes such as a high-temperature mullite membrane Ni/Ni(OH)$_2$, quasi-silver and quasi-platinum types were used. The primary purpose of this electrode investigation was to find a suitable, stable, reproducible and reusable reference electrode in a molten hydroxide electrolyte. Cyclic voltammetry was performed to examine the effect on reaction kinetics and stability to control the working electrode at different scan rate and molten salt temperature. The effect of introducing water to the eutectic molten hydroxide via the Ar gas stream was also investigated. When the potential scan rate was changed from 50 to 150 mV s^{-1}, the reduction current for the

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platinum wire working electrode was not changed with newly prepared nickel reference electrode that designates its stability and reproducibility. Furthermore, increasing the operating temperature of molten hydroxides from 250 to 300 ^{o}C the reduction potential of the prepared nickel reference electrode is slightly positive shifted about 0.02 V. This suggests that it has good stability with temperature variations. The prepared nickel and Pt reference electrode exhibited stable and reliable cyclic voltammetry results with and without the presence of steam in the eutectic molten hydroxide while Ag reference electrode exposed positive shifts of up to 0.1V in the reduction potential. The designed reference electrode had a more stable and effective performance towards controlling the platinum working electrode as compared to the other quasi-reference electrodes. Consequently, splitting steam via molten hydroxides for hydrogen has shown a promising alternative to current technology for hydrogen production that can be used for thermal and electricity generation.

Keywords: Renewable energy; Hydrogen production; Eutectic molten hydroxide; Cyclo voltammetry; Reference electrodes and Platinum working electrode.

1 Introduction

Hydrogen is an efficient energy carrier and emission free candidate to supersede the continuous use of fossil fuels in future because of high mass energy density, fast kinetic rate of electrochemical reaction and only water containing emission gas [1]. Hydrogen gas (H_2) can be produced from biomass gasification, steam reformation of fossil fuel, coal gasification, partial oxidation of hydrocarbons [2] and biomass fermentation [3]. All these resources have environmental issues regarding CO_2 emission, global warming and greenhouse effect [4]. Most of the methods are not green, therefore, electrolysis of water is one of the clean and renewable hydrogen production method. This process has high end-product purity that can reach 99.9 vol% [5] and can be achieved

on both small and large-scale productions [6]. It is considered as promising recyclable green energy carrier because of production of hydrogen without emission of CO_2 [7, 8] that can be used for heating purposes, electricity production, as a fuel for running vehicles [9] and in the fabrication of metal hydride batteries [10].

However, there are existing challenges and barriers in the production of hydrogen gas (H_2), storage and safe transportation [11]. Splitting water is considered flexible, reliable, clean and sustainable method that can produce hydrogen from water electrolysis, sunlight (photoelectrolysis), series of exothermic and endothermic reactions (thermochemical electrolysis). Water electrolysis is preferred over other techniques because yield and efficiency both are quite low for photoelectrolysis and thermochemical electrolysis [12]. H_2 production via water electrolysis included three methods: proton exchange membrane (PEM) electrolysis [13] solid oxide cell electrolysis (SOCE) and alkaline electrolysis [14]. Hydrogen production via molten hydroxide electrolysis is the most scalable technique and it has the main advantage that energy needed for electrolysis is added as heat, which is cheaper than electricity [15]. In addition, this technique can maintain the heat for electrolysis from current passing through electrolyte and the conductivity of hydroxide electrolyte increased with increasing temperature or pressure. All this specification is important for reaction kinetics, that reduced energy loss because of the electrode over potential and increased the system efficiency [5].

The recent research focus is required to increase the efficiency of the electrolysis system and to increase the rate of hydrogen gas production during high-temperature steam electrolysis [16]. However, the formation of hydrogen is influenced by the electrolyte type, concentration, electrode properties, reaction temperature and pressure [17]. There are limited reference electrodes that have

been deemed suitable for a molten hydroxide. Miles et al. [18] explored electrochemically different eutectic molten hydroxides (NaOH-KOH, LiOH-NaOH, LiOH-KOH) using palladium, nickel, silver, aluminium, magnesium, zinc and Li-Fe working electrodes at 250–300 ^{o}C. They suggested the use of Ag/AgCl as a reference electrode because of its faster reaction kinetics in molten hydroxides. Ge et al. [19] investigated the nickel rod quasi-reference electrode for electro-deoxidation of nickel oxide to prepare nickel powder in molten sodium hydroxide at 550 ^{o}C. They were the first to conduct cyclic voltammetry on platinum as a working electrode using molten NaOH at 550 ^{o}C.

The researchers used this material before investigating any other electrodes because of its relatively high chemical stability. The anodic current was due to oxidation and increasing current at cathodic limit can be attributed to the hydrogen evolution reaction. Guo et al. [2] presented the performance and characterisation of a carbon fuel cell using molten hydroxides of NaOH at 550 ^{o}C and NaOH-KOH (54:46 mol%) at 400 ^{o}C. Silver wire was used as a reference electrode in both cases. The study found that the performance of the carbon fuel cell improved with a decrease in temperature up to 400 ^{o}C using the eutectic mixture as an electrolyte. The CoP NA/CC electrocatalyst [20], Pd_4Sn nanochain [21], PdCu clusters [22], PdCo nanodots [23], composite of γ-Fe_2O_3 [24] and 3D macro porous foam of Ni, Cu and FeNi showed high catalytic activity for catalysing reaction at electrodes surface. They exhibited excellent catalytic activity due to high surface area availability and excellent mass transport to the electrode surface [25].

Yang et al. [26] also developed a direct ammonia fuel cell using a platinum electrode and a eutectic electrolytic solution of NaOH-KOH (57–43 mol%). The cell was operated between 200 and 220 ^{o}C and achieved a maximum power of approximately 16 mW cm^{-2}. The cyclic voltammetry of the

platinum electrode was performed with a supply of argon gas or ammonia at 200 ^{o}C and Ag was used as a reference electrode throughout the study. Litcht et al. [1] found in their study that increasing the temperature of molten NaOH or KOH beyond the maximum of 400^{o}C decreased the quantity of water available for hydrogen generation, instead of resulting in the formation of oxides. This increase in temperature also decreased the coulombic efficiency of hydrogen gas. For the combined hydroxide electrolyte (NaOH-KOH; 50–50 mol%), as temperature increased from 200 to 600 ^{o}C, the efficiency of hydrogen gas evolution decreased from 96% to 13.4%. This decrease in hydrogen evolution was due to increment in parasitic side reaction (O^{2-} reduction) with a rise in temperature that competes with hydrogen generation reaction.

Furthermore, Litcht et al. [27] used eutectic molten hydroxide of NaOH-KOH at a 50:50 molar ratio but only for the production of ammonia. They found that it was possible to produce ammonia at an applied voltage of 1.2 V and at a coulombic efficiency of 35% alongside the excess cogeneration of hydrogen. Moreover, the molten hydroxide was also used to develop a direct carbon fuel cell at a low temperature. Hrnciarikova et al. [28] studied the influence of the anode composition: white cast iron (FeC), pure iron (Fe) and silicon-rich steel (FeSi) electrodes on the electrochemical production of ferrate (VI) using molten KOH at temperatures of 110, 130 and 160 ^{o}C. The cyclic voltammetry indicated that the cathodic limit is represented by the evolution of the hydrogen reaction. Subsequently, the anodic limit is represented by the evolution of the oxygen reaction and the anodic peak is represented the melt decomposition. The development of these peaks is dependent upon the operating temperature and the electrode materials used. There are further studies on molten hydroxides that have used platinum wire [29] or copper plated platinum [30] as a quasi-reference electrode respectively.

Zaafarany and Boller [31], investigated the behaviour of a copper electrode in 5 M of NaOH solution electrochemically. The researchers found that the behaviour of the copper electrode in NaOH solution was quite complicated. No simple relations were found between the voltage scan rate and both peaks of current and of potential [31]. Xie et al., [32] explored the Ni_3N@Ni-Bi NS/Ti as electrocatalyst for hydrogen production. It delivered the 10 $mAcm^{-2}$ of current density at 1.95 V of cell potential by using benign condition and non-precious metal catalyst. The most popular electrode material was found nickel as compared Co, Fe, or Cu due to its high catalytic activity, more chemical stability, widespread availability as well as low cost [1].

Different reference electrodes such as Ag/AgCl at low temperature [33] mullite membrane-enclosed Ag/AgCl [2], Graphite-protected silica tube Ag/AgCl [34] and alumina membrane tube Ag/AgCl [35, 36] have been reported as options for high-temperature molten salt. All of these previous studies have not been reported the use of a specifically fabricated reference electrode in the eutectic molten hydroxide. Therefore, this research attempts to fill the gap in knowledge with regards to finding suitable, stable and reusable reference electrodes for molten hydroxide system. In addition, all of the studies reviewed above, an alkaline hydroxide salt was mainly used as an electrolyte to construct the electrolysis cell and be used at both low and high temperatures. There is no direct study as yet which focuses on developing steam electrolysis via eutectic molten hydroxide for hydrogen production through the use of base metals. Therefore, this study mainly contributes to filling this gap and working to increase the efficiency of hydrogen gas using base metals in molten hydroxides.

Therefore, this study has focused on investigating the high-temperature mullite membrane fabricated $Ni/Ni(OH)_2$, quasi-platinum, quasi-silver reference electrodes in eutectic molten

hydroxide. Furthermore, cyclic voltammetry was employed to scan and compare the electrode potential stability and reliability of electrodes. The effect of introducing water to the eutectic molten hydroxide via the Ar gas stream was investigated. This comparison is based on their effect on the reaction kinetics and the stability to control the working electrode at the same operating process conditions. Finding a reliable reference electrode will allow a proper understanding of various working electrode materials that will be used in future. This can eventually lead to a further increase in the electrode kinetics for increasing the hydrogen evolution reaction.

2 Experimental

In this study, various types of reference electrodes such as a high-temperature mullite membrane Ni/Ni$(OH)_2$, quasi-silver and quasi-platinum types were used. The reason for using these different types of reference electrodes was to find a suitable, stable, reproducible and reusable reference electrode. The primary purpose of this electrode investigation is to understand the electrochemical reactions involved during electrolysis in a molten hydroxide electrolyte. When the silver and platinum quasi-reference electrodes were used in this study, these electrodes consisted simply of metal wires with diameters of 1 mm and 0.5 mm respectively. The wires were individually attached to a stainless steel rod 1.5 mm in diameter.

2.1 Preparation of the Ni/Ni$(OH)_2$ reference electrode

The mullite membrane was used to manufacture the reference electrode. The specifications of commercial mullite tube were as 62% Al_2O_3, 36% SiO_2, 500 mm length, 5.0 mm diameter, and 1.0 mm thickness with a minimum bulk density of 2.7 g cm^{-3} with water absorption capacity of 0.02 vol% (Multi-Lab Ltd). 1 mol% Ni$(OH)_2$ (Arcos Organics) was mixed with the eutectic molten hydroxide (NaOH-KOH; 49–51 mol%) (Internal electrolyte, Aldrich) and inserted into the tube

(mullite) forming the internal electrolyte of the reference electrode. Another key point to focus on is the solubility of $Ni(OH)_2$ in molten hydroxides. It was reported by Gayer and Garrett [37] that the solubility of Nickel hydroxide in an alkaline solution of NaOH at 25^{o}C was low, while it was high in any high acidic solution medium. Alternatively, the solubility product of $Ni(OH)_2$ of 6.5×10^{-18} was unchanged when observed from the reaction of nickel hydroxide with either base or acid. A low concentration of 1.0 mol% of $Ni(OH)_2$ in this work was therefore used to make an internal electrolyte mixture of the reference electrode"

The total amount of salt placed in the tube was 1.16 g. The tube was initially placed inside the retort stand but once outside the crucible, it was filled quickly with the prepared mixture of salt to avoid the hydroxides absorbing any moisture from the air. Note that the internal composition of eutectic hydroxides is the same as that of the external electrolyte composition (i.e. the bulk electrolyte used for electrolysis).

The temperature of the furnace was immediately raised above the working temperature of 300 ^{o}C to completely melt the mixed salts in the tube [36]. It should be mentioned here that the mixture was filled into the tube up to a length longer than the uniform heating zone (ca. 12 cm) of the furnace. A nickel (Ni) wire (99.98% pure temper annealed, 0.5 mm diameter, Advent Ltd.) was then inserted to the bottom of the tube containing the electrolyte mixture as the salt began to melt. Subsequently, the tube was sealed and left for 24 h to complete the melting of the salt mixture. Following this, the furnace was cooled to the working temperature so that the upper part of the molten mixture in the tube solidified to seal the tube. Alkaline electrolysis prevents the catalyst requirements and other issues of catalytic metals such as corrosion and ineffective cost. The efficiency of electrolysis system has no need for precious catalytic metal and requires the use of

base metals instead to produce hydrogen gas [32]. This is because the molten hydroxide itself acts as a catalyst during the process. Furthermore, the electrodes have to be resistant to corrosion, have good electric connectivity, exhibit good catalytic properties and maintain a reliable structure during the process [1, 38]. A schematic diagram of the Ni/Ni(OH)$_2$ reference electrode is shown in Fig. 1.

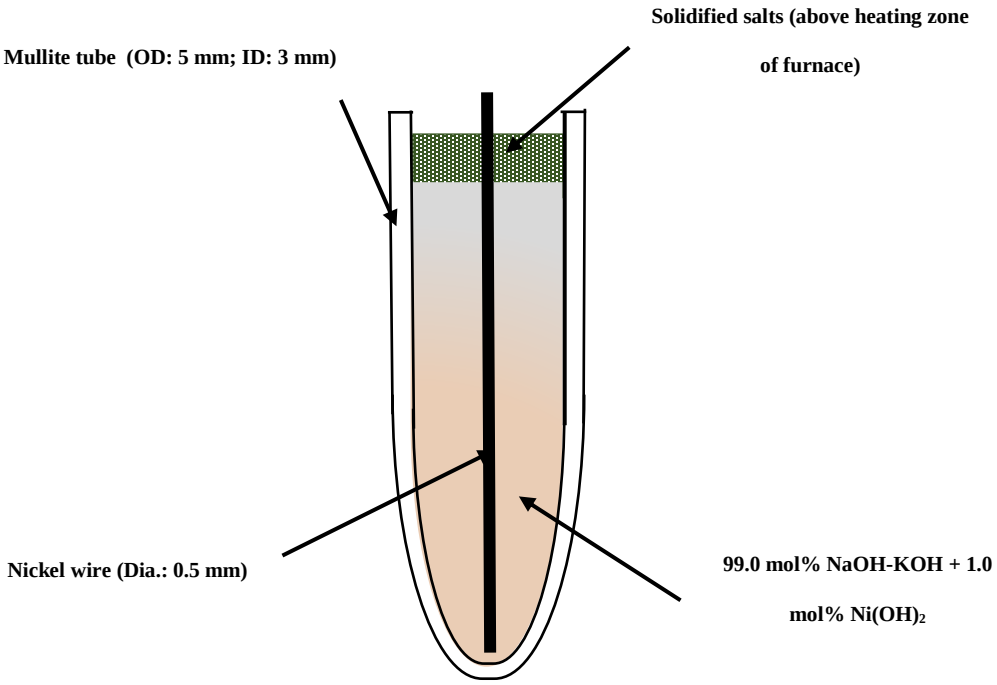


Fig. 1. A schematic of the Ni/Ni(OH)$_2$ reference electrode in a tube membrane.

Performance tests of the nickel reference electrode were conducted in a cylindrical alumina crucible (>99%, 60 mm outer diameter, 120 mm height, 280 mL volume, Almath Crucibles Ltd.) under an argon atmosphere, using an Iviumn-Stat multichannel electrochemical analyser. In all of the experiments, 250 g of the eutectic molten hydroxide (NaOH-KOH; 49–51 mol%) were left under 40 cm^3min^{-1} of argon gas at 300 ^oC for 24 h before use.

2.2 Experimental

Three types of reference electrodes were used in this investigation. Silver wire (99.99% pure temper annealed, 1.0 mm diameter, Advent Research Materials), and platinum wire (99.95% pure temper annealed, 0.5 mm diameter, Advent Research Materials) as quasi-electrode and the mullite membrane $Ni/Ni(OH)_2$ reference electrode. A platinum wire was used as the working electrode, while a stainless steel rod (304 Grade, 5 mm diameter, Unicorn Metals) was used as the counter electrode. In this study, stainless steel was chosen as the counter electrode material due to its inherent stability and good electrical conductivity.

The performance tests were conducted in a cylindrical alumina crucible (>99 %, 60 mm of outer diameter, 120 mm in height, 280 mL in volume, Almath Crucibles Ltd.) under an argon atmosphere; using an Iviumn-Stat multichannel electrochemical analyser. In all experiments, 250 g of the eutectic hydroxide (NaOH-KOH; 49–51 mol%) was left under 40 cm^3min^{-1} of argon gas at 300 ^oC for 24 h before beginning the electrochemical analysis. The furnace was then set to the required experimental temperature.

Subsequently, the working temperature was reduced to the temperature that needs to be examined. However, it was difficult to obtain the exact temperature for electrolyte because it can only be fixed by changing the furnace set temperature. The furnace temperature controller in turn only has an accuracy of ±1 ^oC. The electrolyte temperature was also influenced by additional factors such as the effectiveness of the furnace insulation and the ambient temperature. These factors proved difficult to maintain constant throughout all experiments. CV tests of nickel prepared reference

electrode showed the no change in reduction potential for the formation of NiO_2 at different scan rate. CV tests were carried out using the same reference electrode for 10 days and were repeated thrice. It was found that the lifetime of using the reference electrode is at least 7-9 days to avoid any contamination of internal in the chosen eutectic molten hydroxide. Hence, the ideal ionic membrane to use to construct a reference electrode for the eutectic molten hydroxide is mullite because of its stability, reusability and longer lifetime. Cyclic voltammetry was employed to scan and check the platinum working electrode potential stability and reliability with the three different types of reference electrodes in the eutectic molten hydroxide.

The measurement was made using a platinum wire as a working electrode and one of the reference electrodes (silver wire, platinum wire or the prepared nickel reference electrode). Platinum was used as a working electrode with all reference electrodes before selecting any other working electrode because of its relatively high chemical stability [19]. The immersion depth of the working electrode was ~14 mm. During measurement, the scan started at an open circuit potential, progressing in the negative direction before reversing in a positive direction. The scan rate was varied during the tests and the effect of molten salt temperature was also considered. The steam effect in eutectic molten hydroxide was also studied by cyclic voltammetry. The flow of the water stream was maintained at 7.28 cm^3min^{-1} and it was mixed with argon gas at 40 cm^3min^{-1}. This steam and argon gas mixture were bubbled inside the eutectic molten hydroxide. Cyclic voltammetry plots are expressed in current instead of current density because the platinum working electrode was used at a fixed depth inside the eutectic molten hydroxide through this study [4].

3 Results and discussion

3.1 Standard reaction

Before studying any electrochemical reaction in an alkali hydroxide with or without the presence of water, it is imperative to study the possible reactions that can occur. Additionally, a calculation of the standard reaction potential associated with these reactions must also be made. The possible general reactions in an alkali hydroxide electrochemical process include H_2 and O_2 formation at the cathode and anode respectively (reactions 1–3) [39]. The general reaction of an alkali hydroxide which is in equilibrium with water and metal oxide is shown in reaction 4 [1].

General reaction: $H_2O \rightarrow H_2 + \frac{1}{2} O_2$ (1)

Cathode: $2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ (2)

Anode: $2\ OH^- \rightarrow \frac{1}{2} O_2 + H_2O + 2\ e^-$ (3)

$2\ MOH \leftrightarrow H_2O + M_2O\ \ (M: Na, K)$ (4)

When the general reaction of water (1) is added to the reaction of hydroxide salt (4), the product of this combination generates equivalent yields of hydrogen gas as in reaction (5):

$2\ MOH \rightarrow H_2 + \frac{1}{2} O_2 + M_2O$ (5)

From the reaction (5), it was clear that hydroxide salt was dehydrated and produced a metal oxide, hydrogen and oxygen. For this reason, steam was continuously bubbled inside the eutectic molten hydroxide in order to maintain equilibration hydration of molten hydroxide as steam splitting occurs [1]. The corresponding standard reaction potential of reaction (4) was calculated using HSC

chemistry software (version 6.1; outotec) for the dissociation of the alkali hydroxide NaOH, KOH and the eutectic mixture (NaOH-KOH; 49–51 mol%) as a function of temperature. This is shown in Fig. 2.

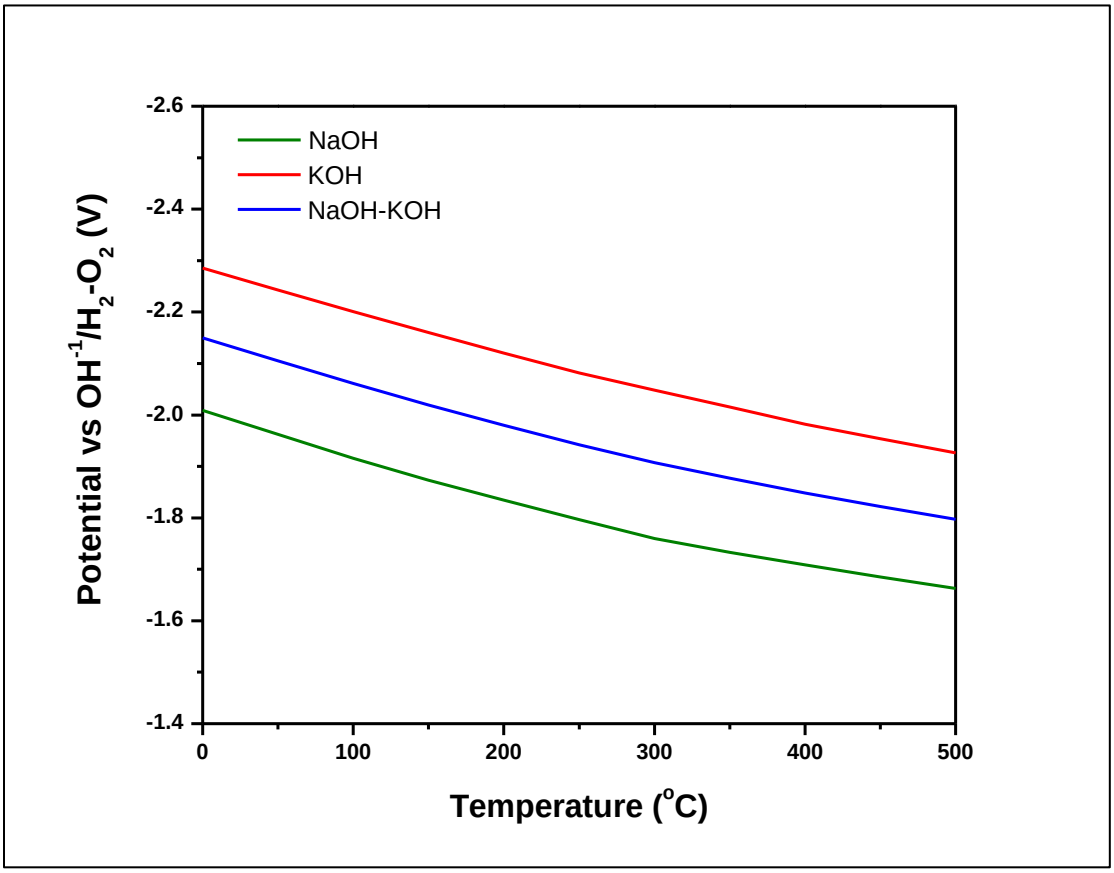


Fig. 2. Standard potential against temperature for the decomposition of molten hydroxides NaOH and KOH; and the eutectic molten hydroxide (NaOH-KOH; 49–51 mol%) into their metal oxides (Na_2O and K_2O), hydrogen gas (H_2) and oxygen gas (O_2). The potential was calculated using HSC chemistry software (version 6.1; outotec) and is reported versus the OH^{-1}/H_2-O_2 reference reaction.

It is obvious from Fig. 2 that the standard reaction potential required for splitting an alkali hydroxide decreases with increasing temperature. In addition, the standard reaction potential for reaction (1) (splitting H_2O to H_2 and O_2) is also calculated using the same software. Fig. 3 shows the comparison between the standard reaction potential of reaction (1) and the standard reaction

potential of a binary mixture of hydroxides at a different temperature. This standard reaction potential gives good information about the minimum energy required to carry out the reaction. The standard potential for the formation of hydrogen gas as observed from Fig. 3 for the decomposition of the eutectic molten hydroxide at 225 ^{o}C is -1.96 V. However, it is -1.06 V from splitting water at the same temperature as shown in Fig. 3.

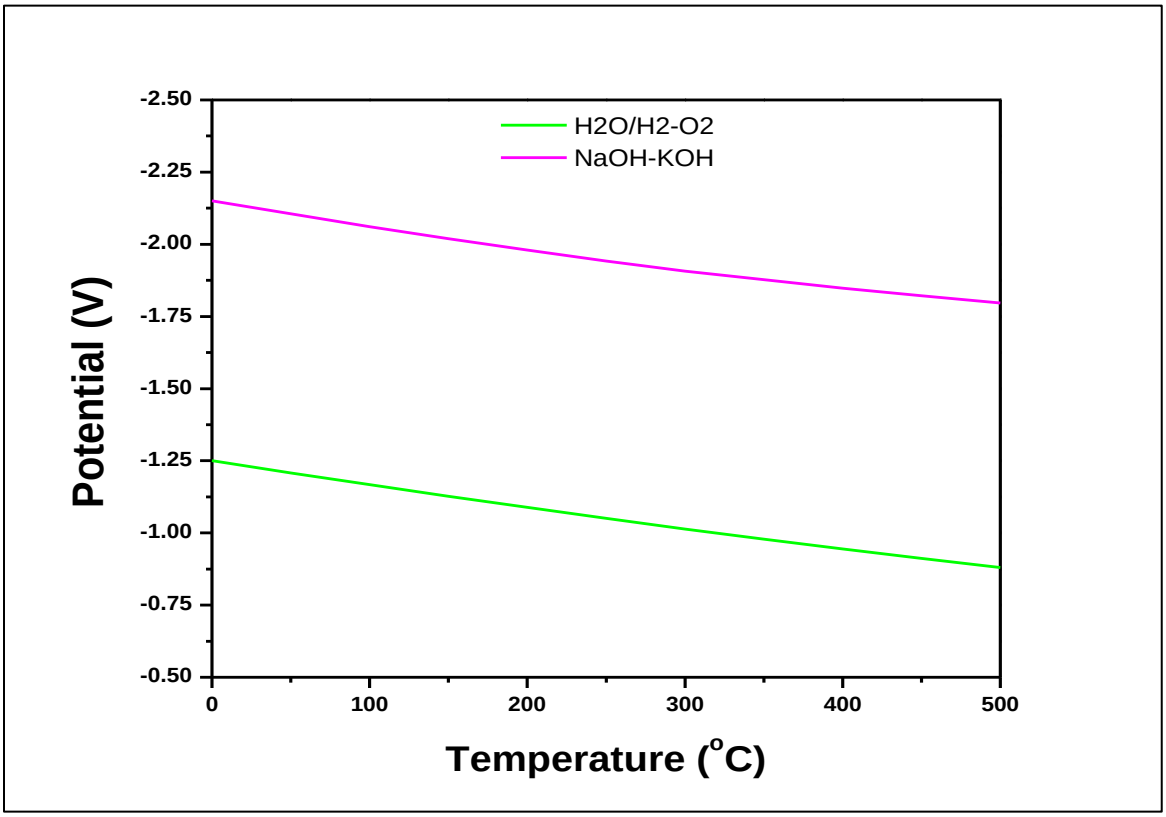


Fig. 3. Comparison between the standard potential of the splitting water (H_2O) into Hydrogen gas (H_2) and oxygen gas (O_2) using the standard potential of decomposition of the eutectic molten hydroxide to their metal oxide (Na_2O and K_2O), hydrogen gas (H_2) and Oxygen gas (O_2) respectively. The potential is calculated using HSC chemistry software (version 6.1; outotec).

3.2 Performance tests of Ag, Pt, and Ni/Ni(OH)$_2$ reference electrodes by cyclic voltammetry

The aim of this electrode investigation was to explore a suitable, stable, reproducible and reusable reference electrode. Different scans were performed only to check the reproducibility and stability of electrodes at same process conditions. Cyclic voltammetry of a platinum working electrode in the eutectic molten hydroxide at 225 ^{o}C was carried out. The first examination used a silver wire as the quasi-reference electrode. Fig. 4 shows the cyclic voltammetry data obtained at a scan rate of 100 mV s^{-1}.

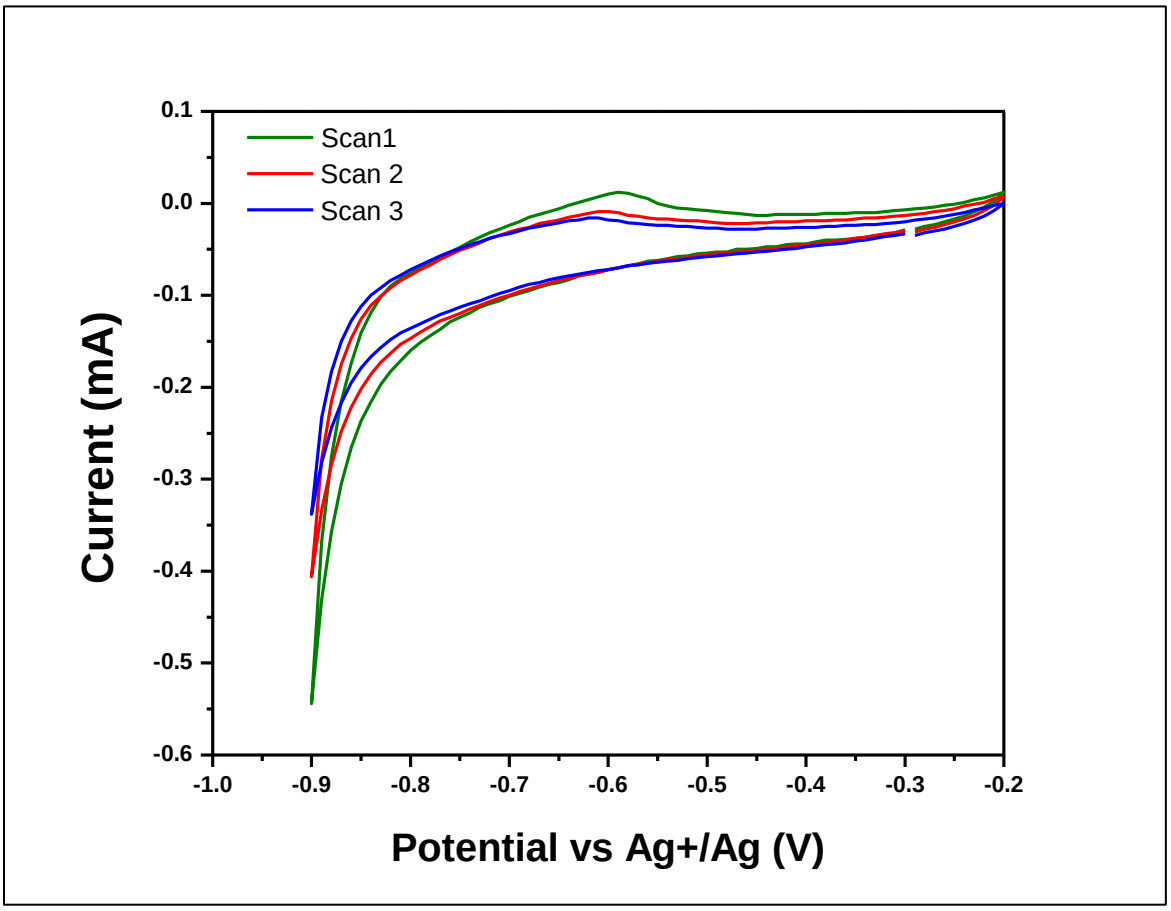


Fig. 4. Cyclic voltammograms of a 0.5 mm Pt wire in the eutectic molten hydroxide; scan rate: 100 mV s^{-1}; CE: 5mm diameter stainless steel rod; an Ar gas atmosphere: 40 cm^{3}min^{-1}. For negative scan limits of -0.9 V RE: 1.0 mm Ag wire; immersion depth: 14 mm.

In Fig. 4, the potential range for cyclic voltammetry scans in this section to test the platinum wire working electrode is set from -0.9 to -0.2 V against the silver reference electrode. Miles et al. [18] reported that the reduction of water at the cathodic limit was -1.3 V vs a silver reference electrode.

$$2H_2O + 2e^- \rightarrow H_2 + 2\,OH^- \quad (6)$$

Yang et al. [26] however, determined that the cathodic limit was -0.9 V vs a silver reference electrode for a setup similar to this study. Therefore, the lower potential limit of -0.9 V vs Ag in this study was used to avoid the negative influence of coexistent hydrogen gas. At the beginning of the forward scan from -0.9 V vs Ag, the reduction current begins at a potential lower than -0.83 V and the current lesser than -0.5 mA. The potential window is kept between -0.83 and -0.2 V which is roughly 0.6 V. Fig. 5 shows the preformed cyclic voltammetry of the platinum working electrode in the eutectic molten hydroxide using a platinum quasi-reference electrode at a temperature of 225 ^{o}C and a scan rate of 100 mV s^{-1}. CV is scanned negatively from -0.85 to 0.0 V as presented in Fig. 5. The cathodic limit reaction from the above figure is influenced by reaction (6) showing water decomposition ($2H_2O + 2e^- \rightarrow H_2 + 2OH^-$). This water is already formed at the anodic limits as reported by Hives et al. [29] who found that the reduction potential limit was about -0.81 V vs Pt. This is in agreement with findings observed from Fig. 5 which exhibit a value of -0.8 V. The potential window of the general reaction (5) ranges between -0.83 and -0.025 V, which is approximately 0.8 V. A prepared nickel reference electrode was also used during the CV investigation on a platinum working electrode at a temperature of 225 ^{o}C and a scan rate of 100 mV s^{-1}. The CV results obtained are displayed in Fig. 6.

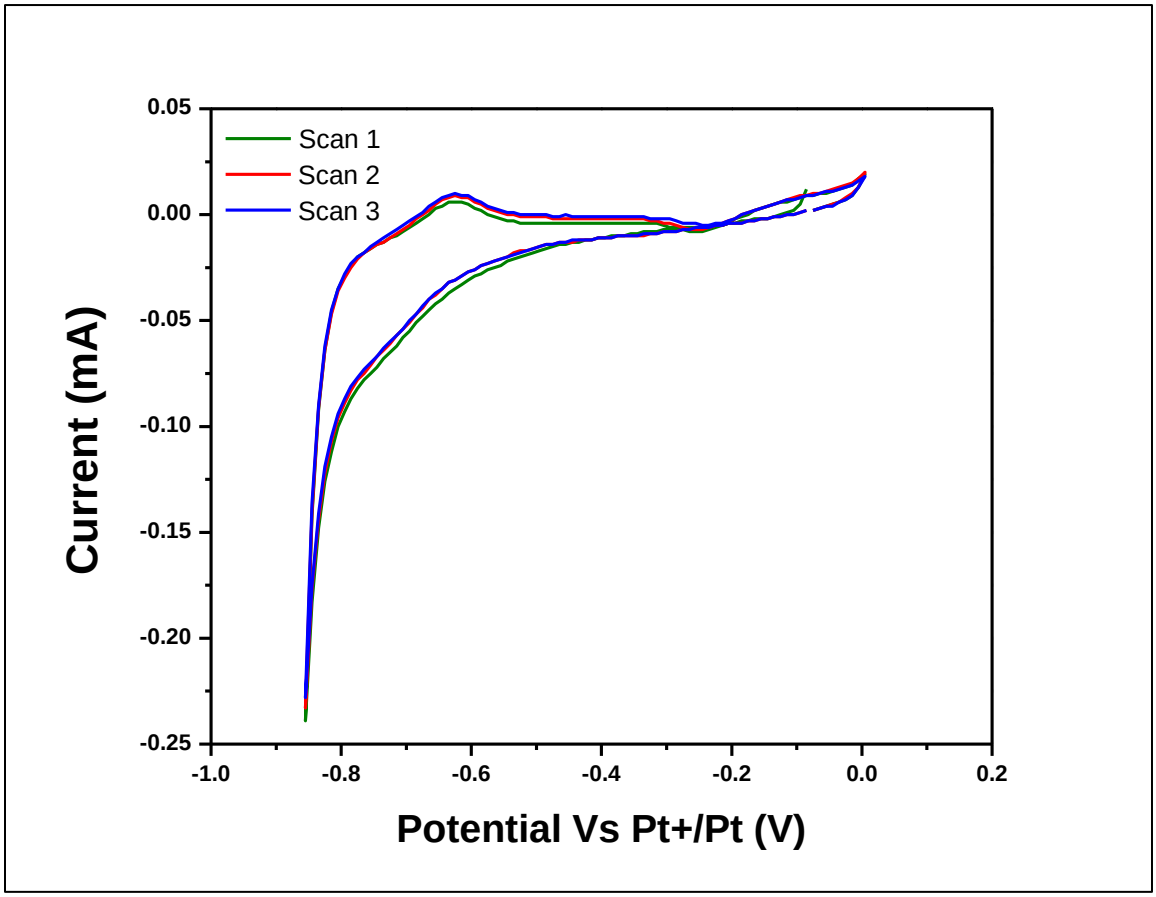


Fig. 5. Cyclic voltammograms of a 0.5 mm Pt wire in the eutectic molten hydroxide; scan rate: 100 mV s^{-1}; CE: 5mm diameter stainless steel rod; an Ar gas atmosphere: 40 cm^3min^{-1}. For negative scan limits of -0.85 V RE: 0.5 mm Pt wire; immersion depth: 14 mm.

In Fig. 6, cyclic voltammetry CV is scanned negatively from -1.0 to 1.0 V vs $Ni/Ni(OH)_2$. The potential for water reduction to hydrogen gas is initiated at -0.69 V versus $Ni/Ni(OH)_2$. This water originates from the oxidation of hydroxide ions at the anodic limits as expressed in ($2OH^- \rightarrow \frac{1}{2}O_2+H_2O+2e^-$) of reaction (3). The electro-stability window of reaction (5) ($2MOH \rightarrow H_2+\frac{1}{2}O_2+M_2O$) is 1.68 V. This result somewhat agrees with the findings in terms of electro stability windows. In the case of the authors, this was reported to be about 1.4 V even though the reduction and the oxidation potential were different from the current study. This difference in the potential can be attributed to a variation in the reference electrode used. Ge et al.

[6] used a nickel rod as a quasi-reference electrode while this study used a prepared mullite membrane Ni/Ni(OH)$_2$ reference electrode to control the working electrode potential.

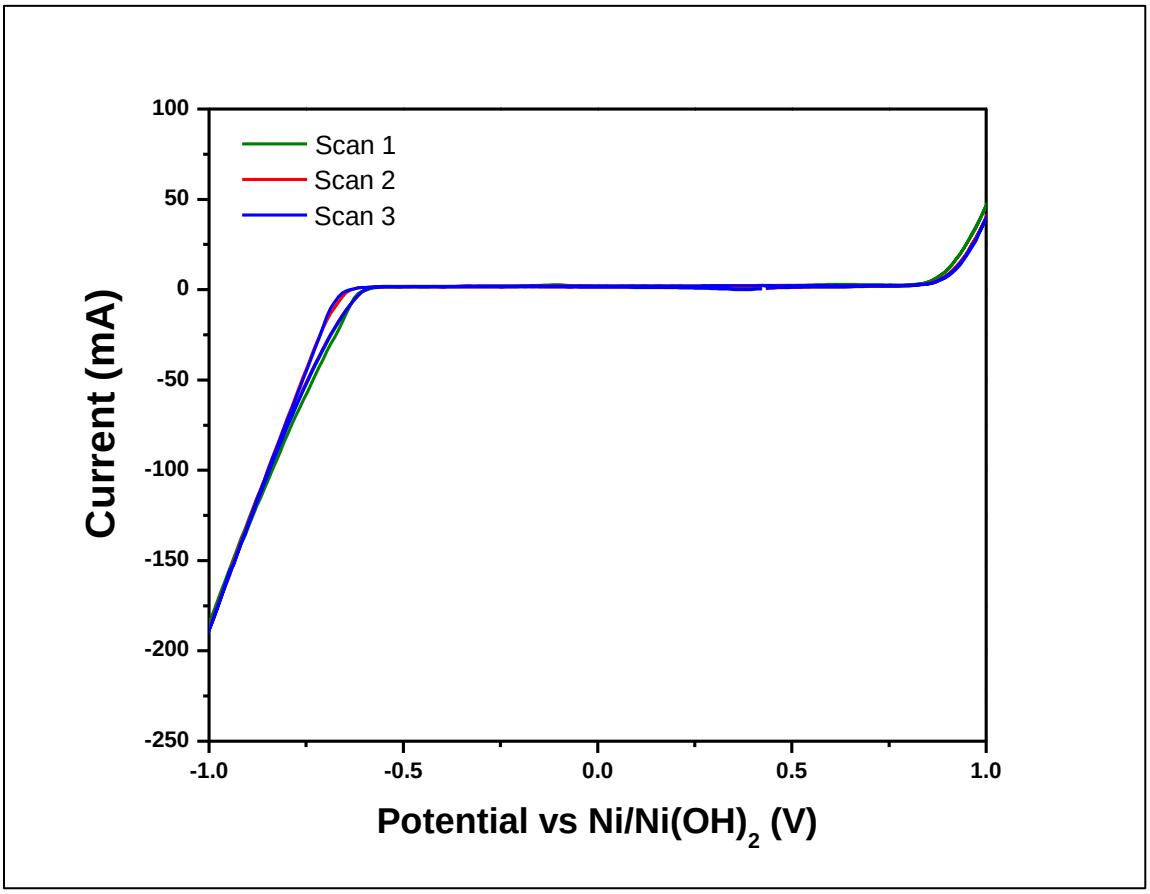


Fig. 6. Cyclic voltammograms of a 0.5 mm Pt wire in the eutectic molten hydroxide; scan rate: 100 mV s-1; CE: 5 mm diameter stainless steel rod; an Ar gas atmosphere: 40 cm^3min^{-1}. For negative scan limits of -1.0 V Ni/Ni(OH)$_2$ in a mullite tube; immersion depth:14 mm

Fig. 4, Fig. 5 and Fig. 6 indicate the potential of working electrode irrespective of the reference electrodes. No cathodic peak or oxidation peak is visible prior to the start of the current wave around the cathodic and anodic limit respectively when the platinum wire was used as a working electrode. This observation indicates that the platinum working electrode was inert in the eutectic molten hydroxide at least within the relatively short experimental time scale considered in this

study. From Fig. 3, the general standard potential for the reduction of hydroxide ions to the hydrogen gas, oxygen gas and oxides of the reaction (5) ($2MOH \rightarrow H_2 + \frac{1}{2} O_2 + M_2O$) is -1.96 V at 225 ^oC. This standard potential is close to -1.68 V vs $Ni/Ni(OH)_2$ as obtained from Fig. 6 which confirm its stability and reproducibility. The comparison of cyclic voltammograms of each reference electrode shows that the prepared nickel has more stability in comparison to silver and platinum quasi-reference electrodes. The Ni3N@Ni-Bi NS/Ti electrocatalyst reported by [32] showed more stability and efficient catalytic activity for 20h. There was no variation in current density after 1000 CV cycles that confirmed its stability as well as durability. Liu et al [40] reported the Ni3N NA/CC as an efficient electrocatalyst for hydrogen evolution because of durable and excellent catalytic activity was observed for 8 hours. It produced 10 mA cm-2 at 1.35 V potential with 1.0 M KOH as well as 0.33 M urea. The nickel prepared reference electrode in the current study has more stability as compared to the above previous studies that was observed for 24h.

3.3 Effect of changing the potential scan rate

Cyclic voltammetry investigations at different potential scan rates were carried out for the platinum working electrode in the eutectic molten hydroxide. This investigation was also carried out using the above-mentioned reference electrodes (silver and platinum quasi-reference electrode, and $Ni/Ni(OH)_2$) to control the working electrode potential. Fig. 7 shows the obtained cyclic voltammetry in the eutectic molten hydroxide at 225 ^oC and at the scan rates ranging between 25 and 150 mV s^{-1}. Silver wire was used as the reference electrode.

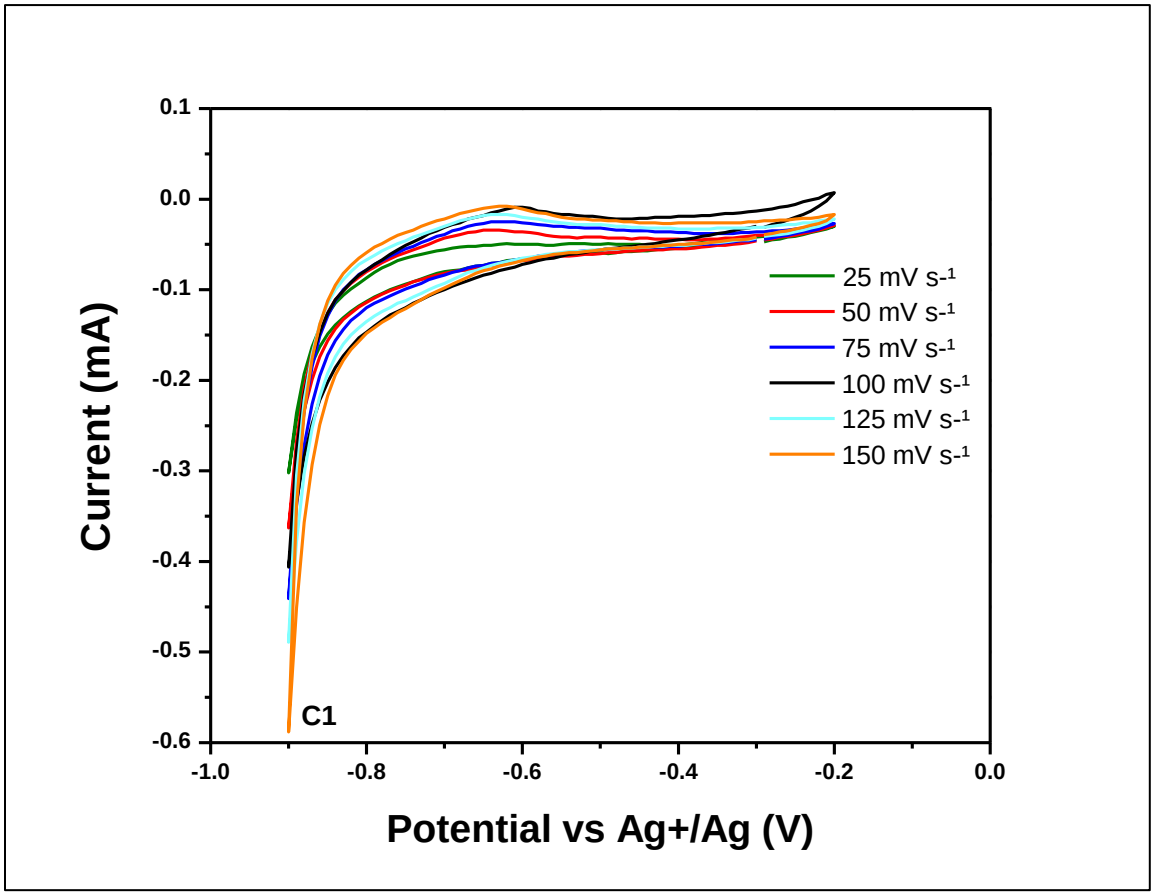


Fig. 7. Cyclic voltammograms of a 0.5 mm Pt wire working electrode in the eutectic molten hydroxide at 225 ^{o}C. For the indicated scan rates; CE: 5 mm diameter stainless steel rod; immersion depth: 14 mm; an Ar gas atmosphere: 40 cm^3min^{-1}; for negative scan limit of -0.9 V, RE: 1.0 mm Ag wire.

The height of the cathodic current at the reduction limit C1 increases with an increase in the speed of the potential scan rate as shown in Fig. 7. The various, recorded reduction currents are summarised in

Table **1**. Using these, obtained results showcase a relationship between the reduction current and the square root of the potential scan rate, demonstrating that mass transport can occur under semi-infinite linear diffusion conditions as in (7):

$$I_R = -0.0998 - 0.0347\, v^{\frac{1}{2}} \quad (R^2 = 0.7849;\ \text{Ag wire}) \qquad (7)$$

Varying the rate at which the Pt working electrode was scanned using a Pt reference electrode, gave similar CVs in Fig. 8 as those obtained for Ag reference electrode.

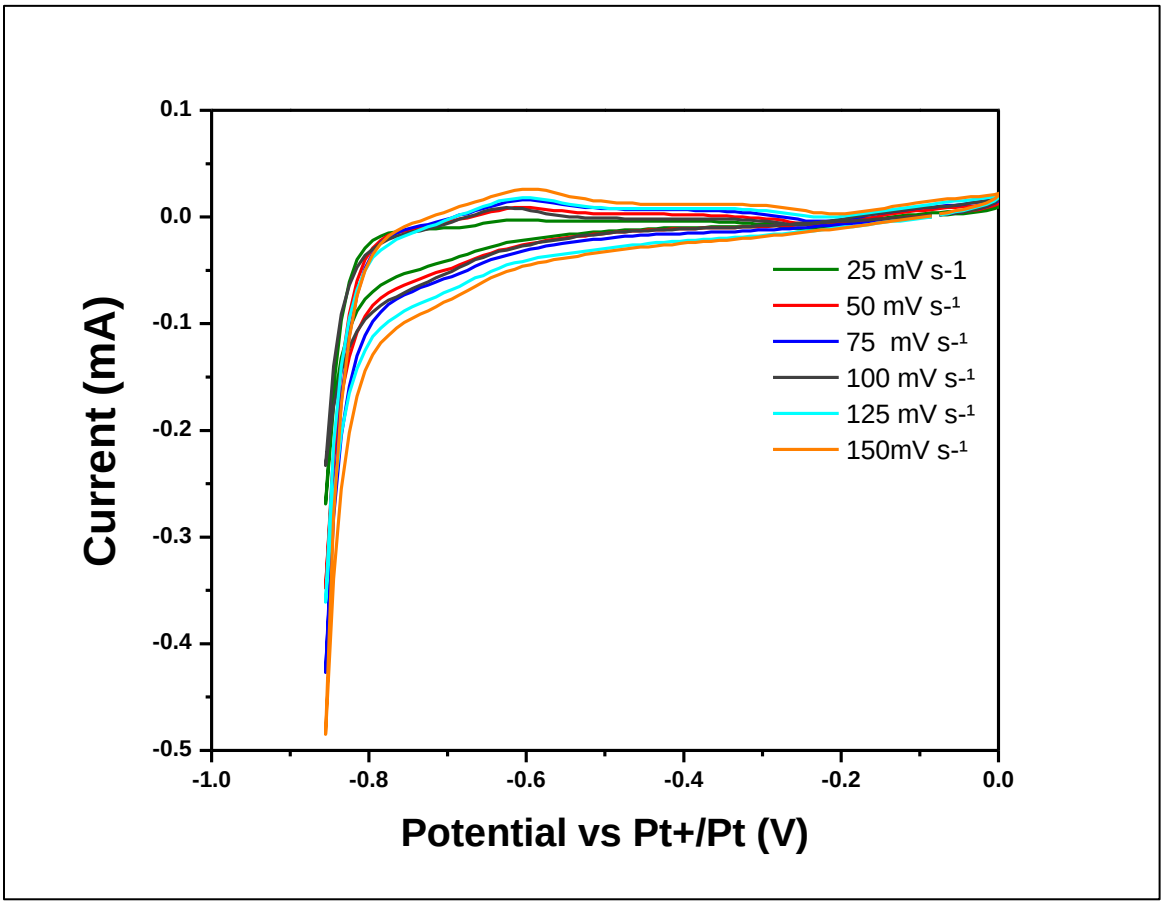


Fig. 8. Cyclic voltammograms of a 0.5 mm Pt wire working electrode in the eutectic molten hydroxide at 225 ºC. For the indicated scan rates; CE: 5 mm diameter stainless steel rod; immersion depth: 14 mm; an Ar gas atmosphere: 40 cm^3min^{-1}; for negative scan limit of -0.85 V, RE: 0.5 mm Pt wire.

The reduction current of the cathodic limit also increased with an increase in the speed of the scan rate. Equation (8) provides the linear relationship between the reduction current and the square root of the scan rate, demonstrating that mass transport can occur under semi-infinite diffusion conditions:

$$I_R = -0.1645 - 0.0211\, v^{\frac{1}{2}} \quad (R^2 = 0.677;\ \text{Pt wire}) \qquad (8)$$

The prepared nickel reference electrode was also used to control the platinum working electrode at the same operating conditions. Hence its stability was compared with the silver and the platinum reference electrodes at different scan rates as shown in Fig. 9.

Table 1. The current limits of a 0.5 mm Pt wire working electrode in the eutectic molten hydroxide at 225 ^{o}C. For the indicated scan rates; CE: 5 mm diameter stainless steel rod; immersion depth: 14 mm; an Ar gas atmosphere: 40 cm^3 min^{-1}.

Scan rate ($mV\ s^{-1}$)	**Ag wire**	**Pt wire**	**$Ni/Ni(OH)_2$**
	cathodic current limit (mA)	cathodic current limit (mA)	cathodic current limit (mA)
25	-0.31	-0.27	-197.50
50	-0.36	-0.34	-198.57
75	-0.33	-0.48	-199.39
100	-0.41	-0.23	-199.41
125	-0.48	-0.36	-199.66
150	-0.58	-0.48	-198.70

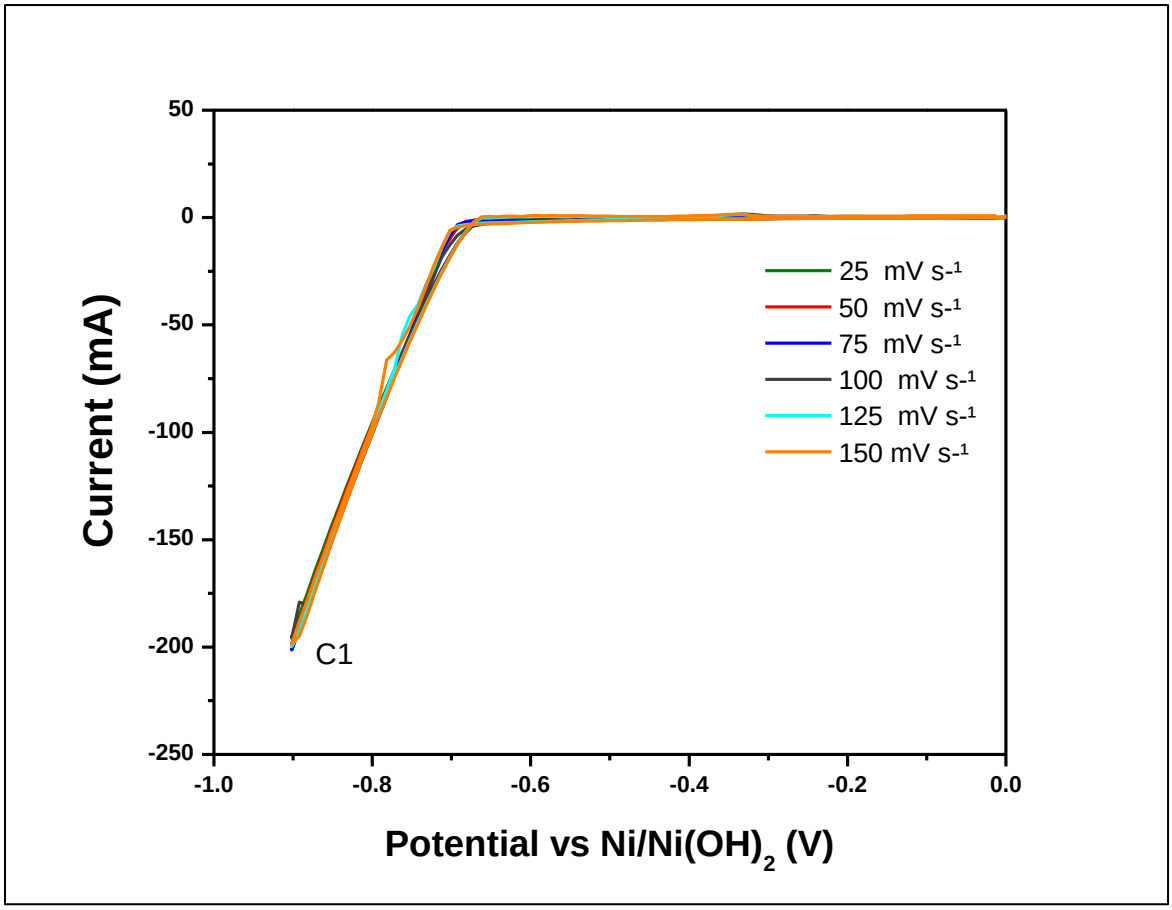


Fig. 9. Cyclic voltammograms of a 0.5 mm Pt wire working electrode in the eutectic molten hydroxide at 225 ^{o}C. For the indicated scan rates; CE: 5 mm diameter stainless steel rod; Immersion Depth: 14 mm; an Ar gas atmosphere: 40 cm^3min^{-1}; for negative scan limit of -0.9 V RE: $Ni/Ni(OH)_2$ in a mullite tube.

The comparison between the reference electrodes was based on checking the stability of the reduction current at different potential scan rates. It is obvious from Fig. 9 with the $Ni/Ni(OH)_2$ reference electrode that the reduction current for the platinum wire working electrode at different scan rates did not change as the scan rate increased. Furthermore, it can be determined that the mass transport reaction between water and the electrode occurs under semi-infinite linear diffusion conditions as in equation (9):

$$I_R = -193.38 - 0.2992\, v^{\frac{1}{2}} \quad \left(R^2 = 0.8799; \frac{Ni}{Ni(OH)_2}\right) \tag{9}$$

In contrast, there is an increase noted in the reduction current as the scan rate increased when either silver or platinum electrodes were used as a reference electrode as observed in Fig. 7 and Fig. 8. However, the prepared nickel reference electrode showed stability in the reduction current and did not show any change with increase the scan rate as shown in Fig. 9 This result further provides evidence regarding the stability of the prepared nickel reference electrode. This stability and reliability of a mullite membrane covering $Ni/Ni(OH)_2$ is attributed to the eutectic molten hydroxide being able to penetrate through and react with the SiO_2; thus forming a stable ion channel between the internal electrolyte ($Ni(OH)_2$-(NaOH-KOH)) and external electrolyte of the eutectic molten hydroxide [41].

3.4 Effect of changing the eutectic molten hydroxide operating temperature

The effect of the eutectic molten hydroxide operating temperature on the cyclic voltammetry studies and hence reference electrode stability was also investigated. A platinum wire was also used as the working electrode in the eutectic molten hydroxide while the reference electrodes were silver, platinum (both wires) and the mullite membrane $Ni/Ni(OH)_2$. Fig. 10 shows cyclic voltammograms obtained at temperatures of 250 and 300 ^{o}C and a scan rate of 100 mV s^{-1} using silver wire as a reference electrode to control the working electrode potential.

From the CVs displayed in Fig. 10, the cathodic limit shifts positively (~0.13 V) between (C2 and C1) as the operating temperature of the eutectic molten hydroxide increases from 250 to 300 ^{o}C. This positive increase in the reduction potential is due to the increase in the operating temperature which in turn affects directly the electrode kinetics. A similar observation was obtained when the

platinum wire was used as the reference electrode as shown in Fig. 11. The recorded reduction potentials for the reference electrodes used are tabulated in

Table **2**. The results clearly indicate a positive shift in the working electrode potential with a molten salt temperature variation of 50 ^{o}C for the Ag and Pt electrodes respectively.

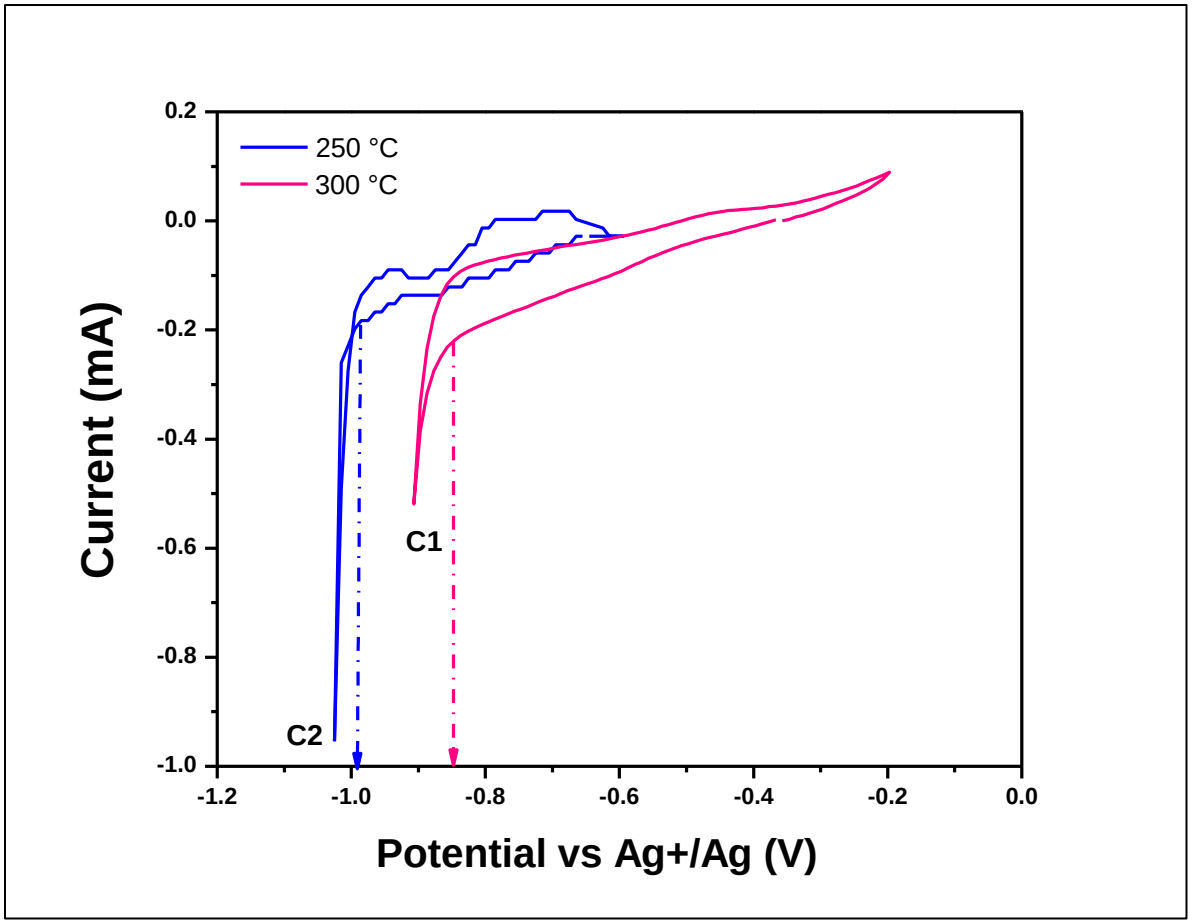


Fig. 10. Cyclic voltammograms of a 0.5 mm Pt wire working electrode in the eutectic molten hydroxide at different operating temperatures and a scan rate of 100 mV s^{-1}; CE: 5 mm diameter stainless steel rod; immersion depth: 14 mm; an Ar gas atmosphere: 40 $cm^3 min^{-1}$. RE: 1.0 mm Ag wire.

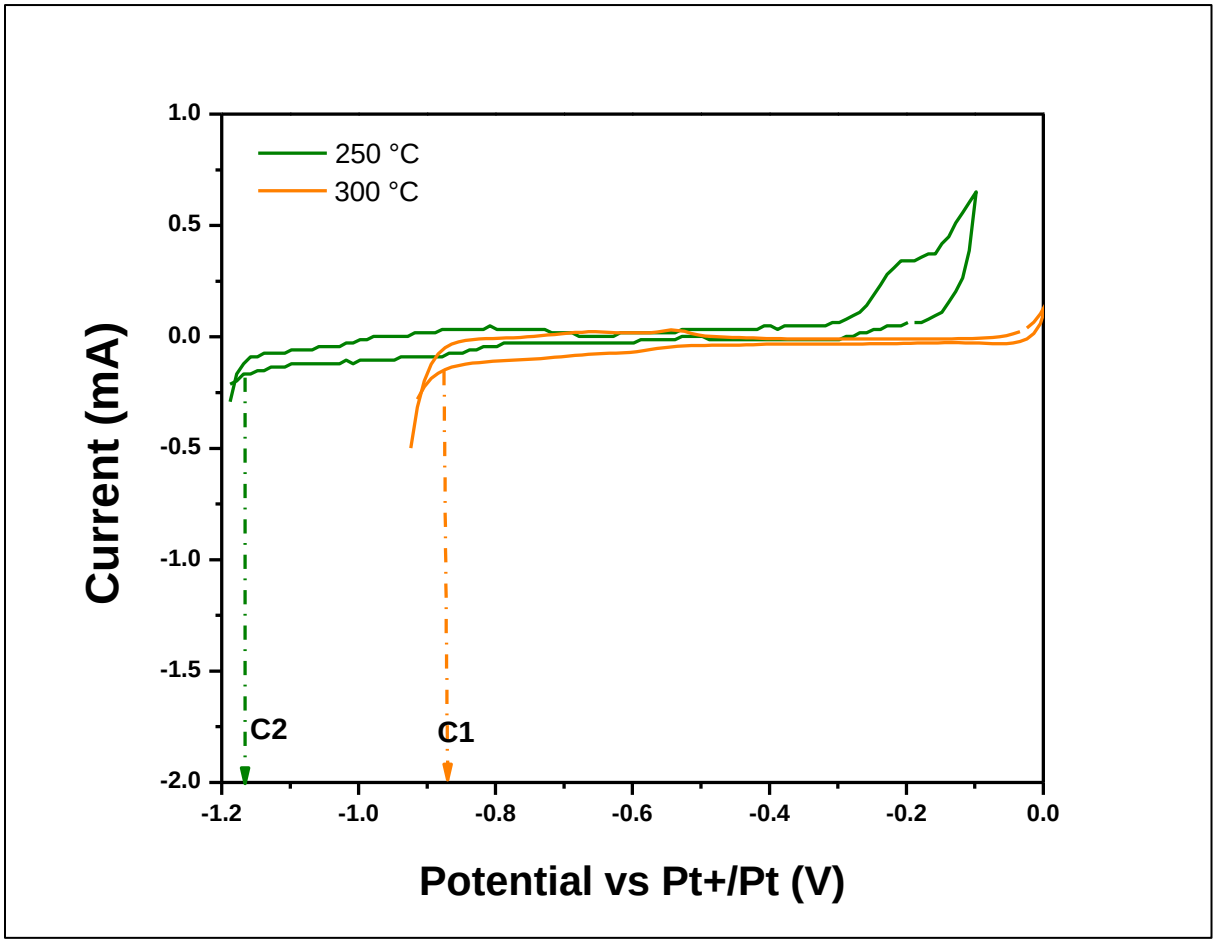


Fig. 11. Cyclic voltammograms of a 0.5 mm Pt wire working electrode in the eutectic molten hydroxide at different temperatures and a scan rate of 100 mV s^{-1}; CE: 5 mm diameter stainless steel rod; immersion depth: 14 mm; an Ar gas atmosphere: 40 cm^3min^{-1}. RE: 0. 5 mm Pt wire.

In the case of the platinum reference electrode, a positive shift of 0.22 V is observed between (C2 and C1) which is 0.1 V higher than when using the silver wire reference electrode at different operating temperature. The platinum reference electrode showed higher potential limit than the silver wire that was due to the increasing order of reduction potential (Ag<Pt) in accordance with electrochemical series. [42]. The reduction potential limit shifts positively by approximately 0.3 V with an increase in temperature as shown in Fig. 11. This positive shift in reduction potential was

due to an increase of temperature that directly influences the electrode kinetics. The recorded reduction potential is illustrated in

Table **2**. The recorded results clearly show that the reduction potential shifts positively with an increase in the temperature of the eutectic molten hydroxide of approximately 50 ^{o}C. The recorded reduction potentials for the reference electrodes used are tabulated in

Table **2**. The results clearly show a positive shift in the working electrode potential with a molten salt temperature variation of 50 ^{o}C for the Ag and Pt electrodes.

Table 2. The reduction potential and current of a 0.5 mm platinum wire working electrode in the eutectic molten hydroxide at various temperatures; with 100 mV s^{-1} scan rate; CE: 5 mm diameter stainless steel rod; immersion depth: 14 mm; an Ar gas atmosphere: 40 cm^3min^{-1}.

Reference electrode	**250 ^{o}C**		**300 ^{o}C**	
	Reduction potential (V)	Current limit (mA)	Reduction potential (V)	Current limit (mA)
Ag wire	-0.99	-0.95	-0.85	-0.52
Pt wire	-1.17	-0.29	-0.87	-0.49
$Ni/Ni(OH)_2$ in a mullite tube	-0.63	-117.37	-0.63	-224.50

Using the $Ni/Ni(OH)_2$ covered with the mullite membrane reference electrode, on the other hand, shows only a slight positive shift in the reduction potential as displayed in Fig. 12 at different operating temperatures and a scan rate of 100 mV s^{-1}. This slight positive shift is due to novel mullite membrane fabrication of $Ni/Ni(OH)_2$ reference electrode.

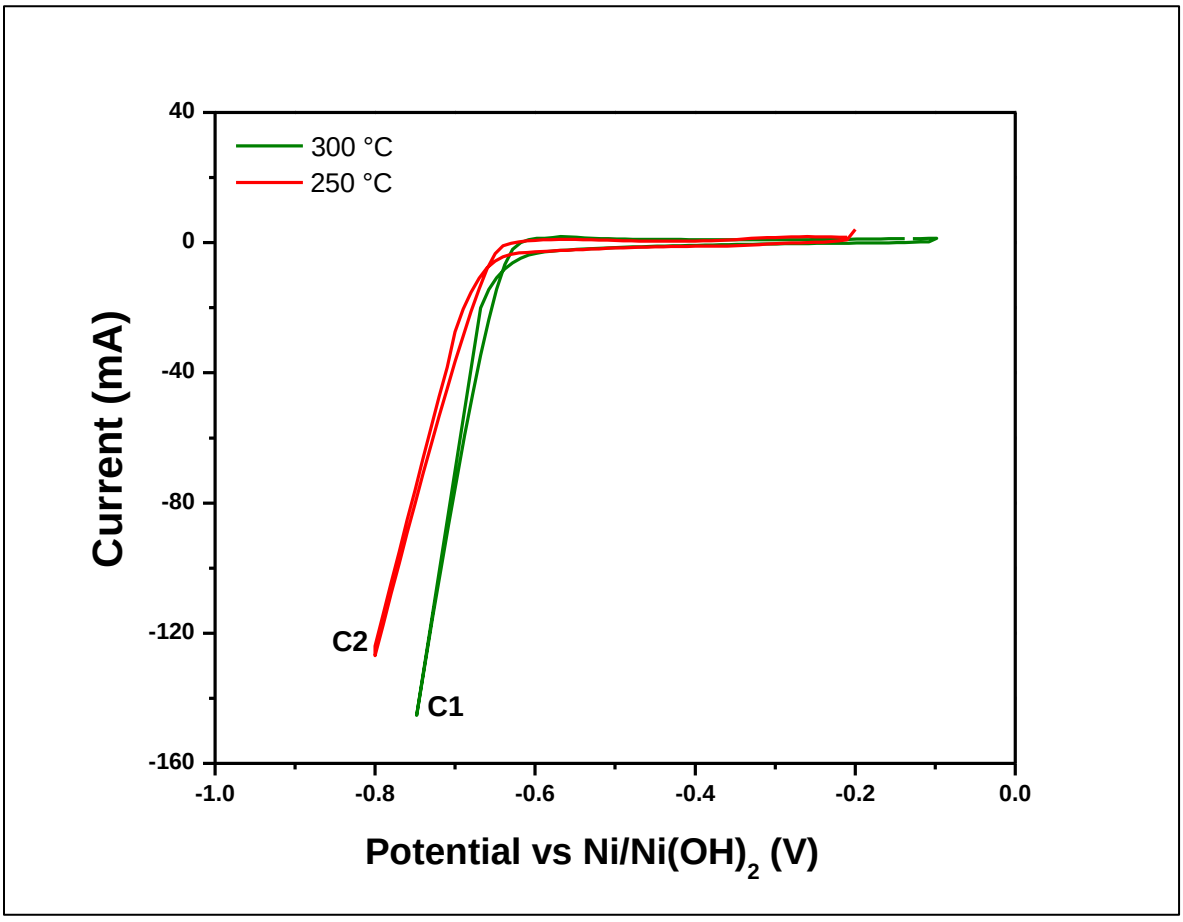


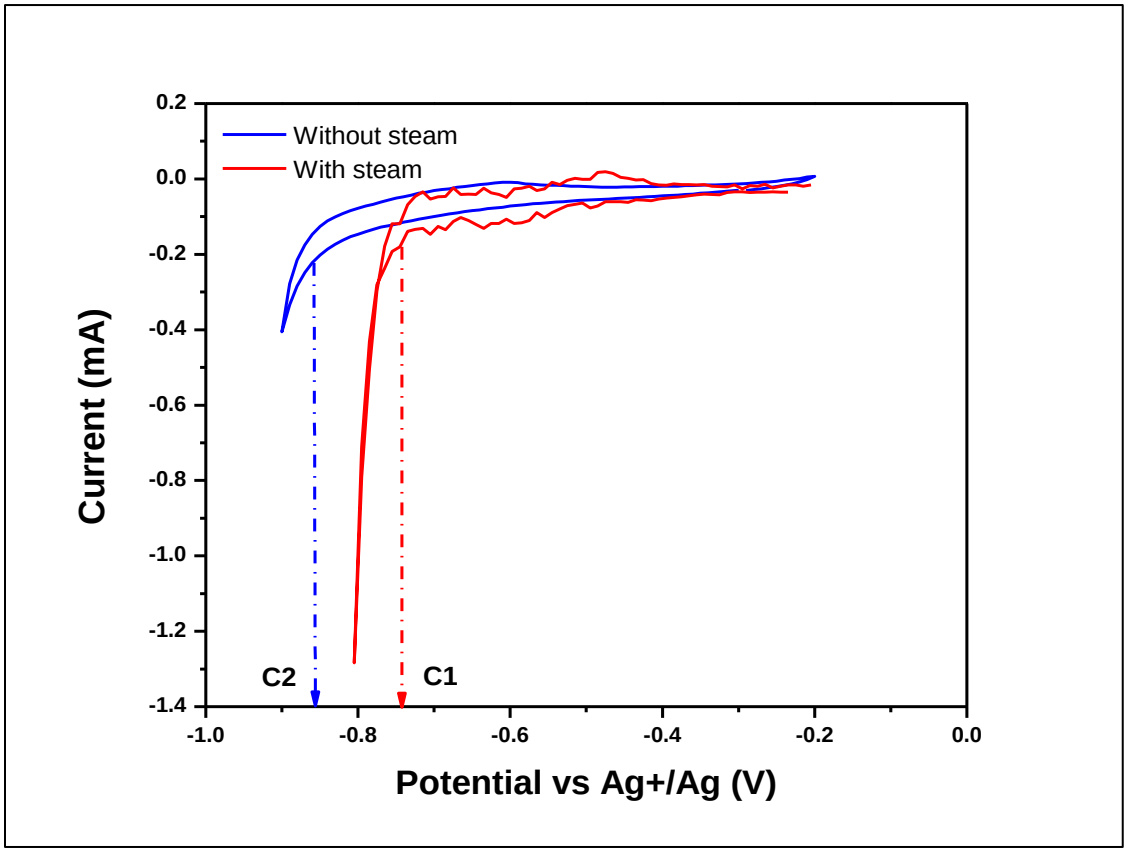
Fig. 12. Cyclic voltammograms of a 0.5 mm Pt wire working electrode in the eutectic molten hydroxide at different temperatures and a scan rate of 100 mV s^{-1}; CE: 5 mm diameter stainless steel rod; immersion depth: 14 mm; an Ar gas atmosphere: 40 cm^3min^{-1}. RE: $Ni/Ni(OH)_2$ in a mullite tube.

The shift in the potential is positive but less than 0.02 V approximately. However, the cathodic limit current increased with an increase in the operating temperature of the eutectic molten hydroxide from -117.37 mA at 250 ^oC (point C2) to -224.62 mA at 300 ^oC (point C1). It can be noted here that the increase in the current of the cathodic limit slightly increased with an increase in the operating temperature. This significant increase in the current of cathodic limit is recorded in

Table **2** and compared with the current of the cathodic limit of other reference electrodes (Ag and Pt). The results of reduction potential and cathodic limit current of Ag, Pt and prepared mullite membrane $Ni/Ni(OH)_{2,}$ reference electrode that is shown in Fig. 10, Fig. 11 and Fig. 12 highlight the stability of the $Ni/Ni(OH)_2$ covered with mullite membrane reference electrode in the eutectic molten hydroxide. Because only a slight positive shift of nearly less than 0.02 V is noted in potential which confirms its stability with the rise of temperature as compared to other reference electrodes. This stability and reliability of the nickel reference electrode covered by a mullite membrane tube can be attributed to the eutectic molten hydroxide penetrating through the membrane and reacting with SiO_2. The latter is one of the substances that is used to construct the mullite tube membrane. Consequently, this membrane forms a stable ion channel through it, acting between the internal reference mixture and outside melt. This observed result in terms of stability due to the freshly prepared nickel reference electrode covered by a mullite tube is different from the result obtained from the Ag and Pt reference electrode. The stability of this reference electrode is confirmed and in accordance with the stability analyses of [43]. Miles, Kissel [44] first discovered that increasing the operating temperature of an alkaline electrolysis cell with nickel-based electrodes allowed for increased electrolyte ionic conductivity and enhanced electrode surface kinetics. However, they also found that the main disadvantage of increasing the cell temperature was the reduced durability of cell materials which came into contact with the corrosive electrolyte. Licht et al [1] reported that KOH mixed molten electrolyte affords maximum 800 $mAcm^{-1}$ of current density at less than 1.7 V of electrolysis potential by increasing temperature from 200 to 600 ^oC. Therefore, the optimum operating temperature of 250 to 300 ^oC was selected for this study.

3.5 Presence of steam in eutectic molten hydroxide

All the cyclic voltammetry investigations were carried out in the eutectic molten hydroxide under a dry Ar atmosphere. Cyclic voltammetry investigations were hence carried out with the presence of steam to study this effect in the eutectic molten hydroxide on the kinetic activity of the working electrode potential. Firstly, argon gas was bubbled through hot H_2O at 70 ^oC. Subsequently, argon left the bottle loaded with H_2O. Then, this wet gas stream entered the retort stand which was already at a temperature >225 ^oC to convert the H_2O in the wet argon to steam. The working electrode used was a platinum wire while the reference electrodes used were Ag and Pt wires, and $Ni/Ni(OH)_2$ covered with a mullite membrane. The molten eutectic hydroxide operating temperature was 225 ^oC and the cyclic voltammetry CV scan rate was 100 mV s^{-1}. Fig. 13 shows the cyclic voltammetry CV of the platinum working electrode obtained with the silver reference electrode with and without the presence of steam.



549

550 **Fig. 13.** Cyclic voltammograms of a 0.5 mm Pt wire working electrode in the eutectic molten hydroxide
551 with and without steam at 225 °C; CE: 5 mm diameter stainless steel rod; RE: 1.0 mm diameter Ag wire;
552 immersion depth: 14 mm; an Ar gas atmosphere: 40 cm^3min^{-1}.
553

554 It is obvious from Fig. 13 that the cathodic limit shifts positively with the presence of steam inside
555 the eutectic molten hydroxide. The reduction potential without the presence of steam is -0.88 V
556 and it shifts positively to -0.75 V with the presence of steam. As can be seen from the figure, a
557 higher reduction current is also observed with the presence of steam inside the eutectic molten
558 hydroxide. This rise in reduction current was due to steam that contributes to the electrode
559 reduction process and enhanced the hydrogen evolution rate at working electrode [27].

560 Table **3** summarises the reduction potential and the current at the cathodic limit achieved with and
561 without the presence of steam insides the eutectic molten hydroxide. The current at the cathodic
562 limit increases from -0.41 mA at C2 to -1.26 mA at C1 with the presence of steam. This increase

in the current suggests that the presence of steam contributes to the reduction process and hence increases the production rate of hydrogen gas formed at the working electrode (cathode). Fig. 14 shows the platinum working electrode cyclic voltammetry with and without steam at the eutectic molten hydroxide operating temperature of 300 ^{o}C using platinum wire as the quasi-reference electrode.

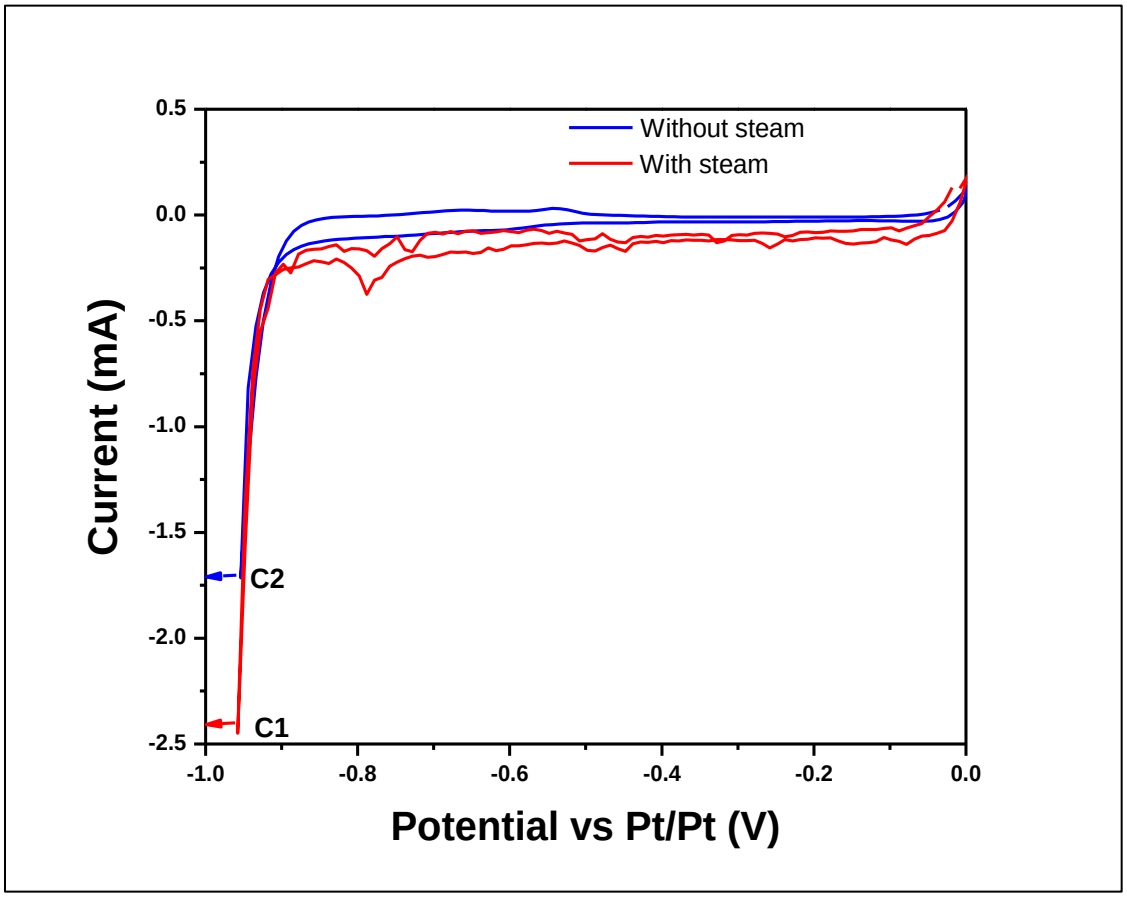


Fig. 14. Cyclic voltammograms of a 0.5 mm Pt wire working electrode in the eutectic molten hydroxide with and without steam at 300 ^{o}C; CE: 5 mm diameter stainless steel rod; RE: 0.5 mm Pt wire; immersion depth: 14 mm; an Ar gas atmosphere: 40 cm^3min^{-1}.

Unlike the silver electrode, the platinum reference electrode showed no obvious difference in the reduction potential with and without the presence of steam inside the eutectic molten hydroxide.

In the presence of steam, however, the production rate of hydrogen gas likely increased as noticed by the increase in current at the cathodic limit C1 (see Fig. 14). In this case, the current increases from -1.75 mA (without steam at C2) to -2.5 mA (with steam at C1) as reported also in Table **3**. Litch et al., [1] examined a wide range of pure and mixed hydroxide electrolytes such as LiOH, KOH, NaOH, $Ba(OH)_2$ and NaOH-KOH at temperatures ranging from 200 to 700 ^oC. They also used steam and an argon gas stream inside the electrolyte.

Table 3. The reduction potential and the current limit produced with and without the presence of steam in the eutectic molten hydroxide. WE: 0.5 mm Pt wire; CE: 5 mm Stainless steel rod; and RE:1mm Ag wire at 225 ^oC, 0.5 mm Pt wire at 300 ^oC and $Ni/Ni(OH)_2$ at 225; immersion depth: 14 mm; an Ar gas atmosphere at 40 cm^3min^{-1}.

Reference electrode	**Without steam**		**With steam**	
	Reduction potential (V)	Current limit (mA)	Reduction potential (V)	Current limit (mA)
Ag wire	-0.86	-0.41	-0.76	-1.28
Pt wire	-0.88	-1.57	-0.88	-2.45
$Ni/Ni(OH)_2$	-0.67	-196.01	-0.66	-217.50

Cyclic voltammetry scans using $Ni/Ni(OH)_2$ reference electrode is displayed in Fig. 15. The operating temperature during the test was 225 ^oC, the working electrode was Pt wire and the scan rate was maintained at 100 mV s^{-1}. The electrochemical behaviour of the working electrode was the same with and without presence steam as shown in Fig. 15. The reduction potential of prepared nickel electrode for hydrogen gas formation is still the same at -0.67 V with and without steam. Therefore, the platinum working electrode controlled by the prepared $Ni/Ni(OH)_2$ reference electrode produces stable cyclic voltammetry results even when water is found in the eutectic molten hydroxide.

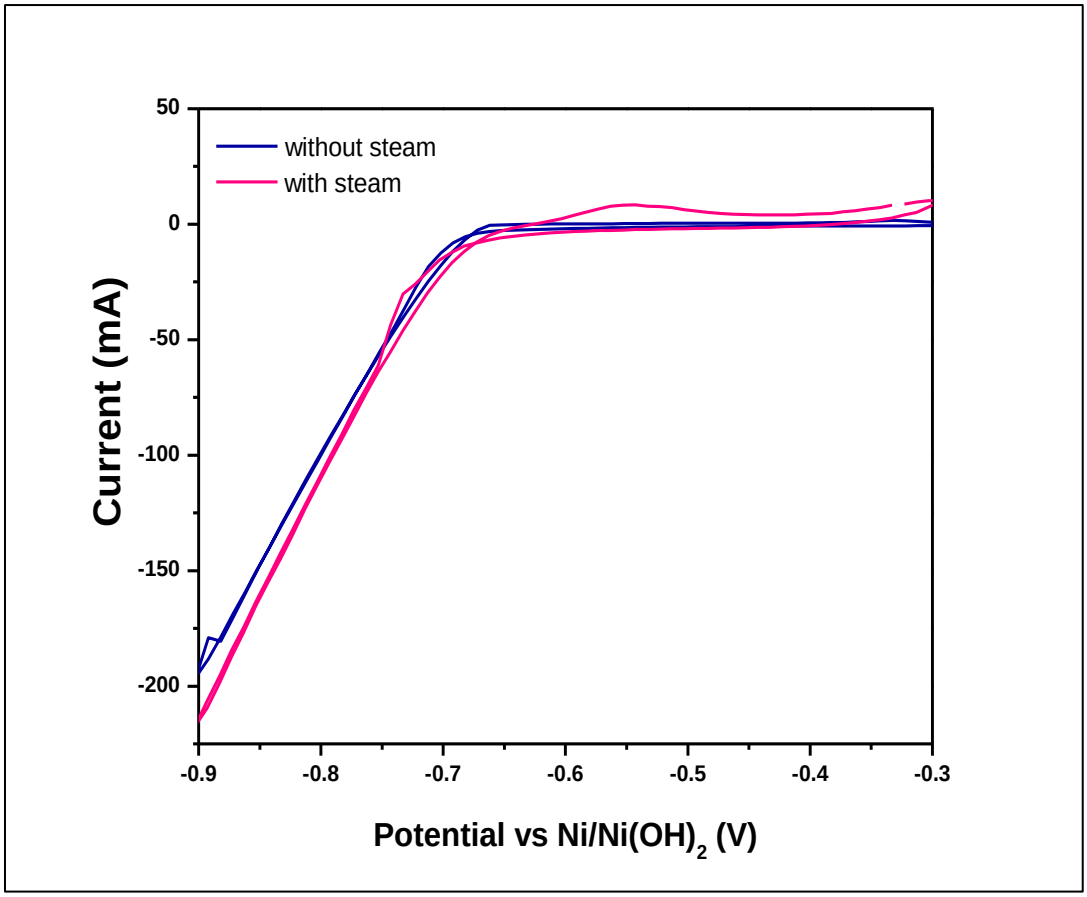


Fig. 15. Cyclic voltammograms of a 0.5 mm Pt wire working electrode in the eutectic molten hydroxide with and without steam at an operating temperature of 225 ^{o}C and a scan rate of 100 mV s^{-1}; CE: 5mm diameter stainless steel rod; RE: $Ni/Ni(OH)_2$ in a mullite tube; Immersion Depth: 14 mm; an Ar gas atmosphere:40 cm^3min^{-1}.

In general, the presence of steam inside the eutectic molten hydroxide increases slightly the value of the cathodic limit current implying an increase in the yield of hydrogen gas. This stable reduction potential behaviour is also similar to that obtained using the platinum reference electrode. In terms of gas produced, however, the cathodic current obtained when the Pt reference electrode was used is only -2.5 mA while that for the $Ni/Ni(OH)_2$ electrode is -217.3 mA. This observed current indicates that the latter has a higher evolution of the hydrogen gas reaction than without the presence of steam [27]. In other words, the $Ni/Ni(OH)_2$ covered with a mullite membrane reference

610 electrode designed in this research has proven to be very stable in effectively controlling the
611 potential of the Platinum working electrode. This leads to a high cathodic product (hydrogen gas).

612 ## 4. Conclusions

613 A new reference electrode for eutectic molten hydroxide was fabricated by covering $Ni/Ni(OH)_2$
614 with an ionic membrane of mullite tube. The prepared reference electrode was compared with silver
615 and platinum quasi−reference electrodes in the same operating conditions. The findings of this
616 work can be summarised as follows:

617 • Eutectic molten hydroxide (NaOH-KOH; 49–51 mol%) at 225 ^{o}C is -1.96 V and this was
618 calculated using HSC chemistry software (version6.1; outotec).
619 • The cyclic voltammetry investigation shows that when the potential scan rate was changed,
620 the current limit changed and this change in current confirmed that mass transport can occur
621 under semi-infinite linear diffusion conditions at the cathodic limit of the platinum working
622 electrode.
623 • One of the more significant findings to emerge from this study is that increasing the
624 operating temperature of molten hydroxides by about 50^{o}C shifted the reduction potential
625 of both silver and platinum reference electrodes. However, only a slight positive shift of
626 0.02 V was observed with prepared $Ni/Ni(OH)_2$ covered with a mullite membrane that
627 suggests it has good stability as temperature varies.
628 • The results also indicate that the prepared nickel and platinum reference electrode can be
629 used to control the platinum working electrode, thereby producing stable and reliable cyclic
630 voltammetry results with and without the presence of steam in the eutectic molten

hydroxide. The silver reference electrode, on the other hand, showed positive shifts of up to 0.1V in the reduction potential.

- From above results, it can be concluded that the $Ni/Ni(OH)_2$ covered with a mullite membrane reference electrode compared with Ag and Pt reference electrode has shown to be very stable in effectively controlling the potential of the Platinum working electrode. This subsequently leads to a high cathodic product yield (hydrogen gas). Therefore, effective control of the working electrode by the stable reference electrode directly contributes to increasing the hydrogen gas evolution reaction through constructing a stable ion channel.

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