Electrochemical study of different membrane materials for the fabrication of stable, reproducible and reusable reference electrode

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Abstract

Fabrication of stable, reproducible and reusable reference electrodes for low energy and high-temperature steam splitting is of great interest for hydrogen fuel production without anthropogenic carbon dioxide (CO_2) emission. This study has been conducted for the detection of suitable material for the fabrication of novel reference electrode. In the present scenario, this research is designed to fabricate a novel nickel reference electrode by using operating conditions of eutectic molten hydroxide (NaOH-KOH, 49–51 mol%) at temperature 300 °C in an ion-conducting membrane of alumina and mullite tube. Afterwards, the designed nickel reference electrode has been examined for its reusability and stability by using electrochemical technique and cyclic voltammetry. Five scans of cyclic voltammetry are performed for both membrane fabricated reference electrode. A slight positive shift in oxidation peaks is observed for mullite membrane electrode (64 mV from scan 1 to 5). The stability measurements are noted by changing the scan rate between 50 and 150 mV s^{-1}. Furthermore, the results show that the $Ni/Ni(OH)_2$ reference electrode covered with a mullite membrane is stable and reusable at 300 °C temperature without any deterioration. The stability and reusability of prepared nickel

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reference electrode covered by mullite tube in the eutectic molten hydroxide were up to 9 days to carry out an electrochemical investigation, while for alumina tube reference electrode the stability and reliability were up to 3 days. The internal electrolytic material and ionic conductance can play an important role for future studies with this reference electrode along with optimisation of temperature and scan rate parameters.

Keywords: Renewable energy; Hydrogen production; Electrode process; Cyclic voltammetry; Reference electrode and Molten salts.

1. Introduction

Hydrogen (H_2) is considered to be one of the most promising and vital fuels for future because of its remarkable capability of reducing air pollution. It can overcome the problem that may be caused by the depletion of fossil fuels. It is a high-efficiency energy carrier and has technically shown that it can be used for transportation, heating and power generation. It has the potential to replace current fuels in all present applications [1]. One of the most popular technologies that are used to produce hydrogen fuel is steam reforming and gasification from the feedstock of fossil fuels [2]. Some industries also produce hydrogen from biomass via reforming, gasification and fermentation [3, 4].

H_2 gas can be produced from either non-renewable conventional energy sources such as; hydrocarbon, natural gas and coal or from renewable energy sources such as; hydropower, solar energy, wind and biomass [5, 6]. It is documented that a large reduction in the release of harmful emissions will occur if hydrogen is produced from renewable energy resources [7]. Electrolysis is the most common method that is used to produce H_2 gas using water as a clean and renewable energy resource [8]. This process has high end-product purity that can reach up to 99.9 vol% and can be achieved on both small and large-scale productions [9]. The materials used to construct the electrolysis cell must also withstand certain tough operating conditions and need further development in order to commercialise this clean energy method for producing hydrogen gas as a fuel [10]. Furthermore, H_2 has received focus from among several alternative fuel sources because it provides the highest potential benefits and fulfils most of the criteria required for an ideal fuel. Hydrogen fuel is similar to electricity in terms of being a high-efficiency energy carrier when it is used. Moreover, it can lead to zero or near-zero greenhouse gas emissions. For this reason, recently, many researchers and organisations have promoted hydrogen fuel as a solution to global warming. Hydrogen is potentially emissionsfree alternative to fossil fuels, it has a very high specific energy content of about 140 MJ kg^{-1} in comparison to gasoline which has a value of 48.6 MJ kg^{-1} [11].

Hydrogen can be produced directly from splitting water using different techniques. These techniques include; photoelectrochemical hydrogen production (photoelectrolysis), thermochemical water splitting and water electrolysis [12]. Recent researches focus on using electrolysis to split water into its core components of hydrogen and oxygen in the gaseous form. Water splitting via molten hydroxide electrolysis has several advantages [13] including; ion conduction, heat, wide electrochemical window and fast reaction kinetics [14]. The main advantage is that a significant part of the energy needed for electrolysis is added as heat, which is cheaper than electricity. Furthermore, the conductivity of hydroxide electrolyte is very good at high temperature and increases with an increase in temperature. This electrolyte specification is important for accelerating reaction kinetics, reducing energy loss due to electrode over potential and therefore increasing the overall system efficiency.

In addition, this technology do not require precious catalytic metal use as a base metal to produce hydrogen gas. This is because the molten hydroxide itself acts as a catalyst during the process [15]. The required decomposition potential of water is also reduced because of the high operating temperature of molten salt. For long-term use, if the electrolysis system is well isolated, the energy consumed is consistently reduced. Furthermore, molten salt does not need any additional heat because it maintains the required heat from the current passing through during electrolysis process if the system is well isolated. Researchers are exploring this field these days very deeply for the optimisation of conditions to produce hydrogen gas [7, 16]. Selecting a suitable membrane material in molten hydroxide is considered very important. The designed reference electrode contains a membrane, an electrolyte and a nickel wire. Selecting the right ionic membrane is important in designing the reference electrode and these membranes must have good chemical and electrochemical stability, reproducibility and reusability [17].

There is a lack of literature regarding the choice of suitable membrane materials for an adequate reference electrode in the case of molten hydroxides. Miles et al. [18] stated that not a single reference electrode has been established for molten hydroxide system. Different reference electrodes such as PTFE membrane-enclosed Cu^+/Cu in NaOH-KOH [19], quartz, pyrex, porcelain, mullite membrane-enclosed Ag/AgCl [20-22], graphite-protected silica tube Ag/AgCl [23] and alumina membrane tube Ag/AgCl [24, 25] have been reported as options for high-temperature molten salt. The study of Wang et al. [25] examined a Ag/AgCl reference electrode in an alumina tube membrane using different types of molten salts such as $CaCl_2$, $CaCl_2$-LiCl, $CaCl_2$-NaCl, $CaCl_2$-LiCl-KCl, Li_2CO_3-K_2CO_3. Another study conducted by Ge et al. [26] used a nickel rod quasi-reference electrode to test in molten NaOH. None of these previous studies used a proper, specifically prepared reference electrode in the molten hydroxide. Hence, this study is focused on investigating the best prepared nickel reference electrode for eutectic molten hydroxide. Ni metal was selected instead of Ag, Co, Cu and Fe because of its easy availability, cheapness, high catalytic activity and lower corrosion effects [14]. Researchers studied Cu electrode electrochemical potentials in 5 M solution of NaOH. A series of complex redox reactions have been reported with Cu electrode [27].

Another key point to focus on is the solubility of $Ni(OH)_2$ in molten hydroxides. It was reported by Gayer and Garrett [28] that the solubility of nickel hydroxide in an alkaline solution of NaOH at 25 ^oC was 6×10^{-5}, 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. Furthermore, $Ni(OH)_2$ has been reported as an interesting co-catalyst [29] and enhances the electrical conductivity of the reaction [30]. Therefore, a low concentration of 1 mol% of $Ni(OH)_2$ in this work is used to make an internal electrolyte mixture of the reference electrode.

This study attempts to fill the gap in the research to find suitable, stable and reusable reference electrodes for molten hydroxides. The study has been performed on a laboratory scale. Two different types of material have been investigated including alumina membrane (Al_2O_3) and mullite membrane ($3Al_2O_3.2SiO_2$) for the fabrication of a desired reference electrode. Then a comparison has been made between both materials to find out which one is more suitable. Furthermore, different parameters have been tested for the optimisation study including temperature, scan rate and time. The cyclic voltammetry electrochemical technique was used to study the stability and reusability of the prepared reference electrode covered with an ionic membrane.

2. Experimental

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

Two types of membrane; alumina and mullite were used to manufacture reference electrodes. The specifications of commercial alumina tube were as 99.7% Al_2O_3, 500 mm length, 5 mm external diameter and 1 mm wall thickness with a minimum bulk density of 3.92 g cm^{-3} and a water absorption capacity of 0.01 vol% (Multi-Lab Ltd). On the other hand, the mullite tube of 62% Al_2O_3, 36% SiO_2, 500 mm length, 5 mm diameter and 1.0 mm thickness had 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 (alumina or mullite) forming the internal electrolyte 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 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 was 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. Moreover, 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 into the bottom of the tube as salt began to melt. Subsequently, the tube was sealed and left for 24 h to complete the melting of the salt mixture at 300 ^{o}C. Following this, the furnace was cooled to the working temperature so that the upper part of the molten mixture in the tube is solidified to seal the tube. A schematic diagram of the $Ni/Ni(OH)_2$ reference electrode is shown in Fig. 1.

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 multi-channel electrochemical analyser. In all of the experiments, 250 g of the eutectic molten hydroxide (NaOH-KOH, 49–51 mol%) were left under 40 cm^3 min^{-1} of argon gas at 300 ^{o}C for 24 h before use. The schematic diagram of the experimental setup is shown in Fig. 2.

The cyclic voltammetry technique was used to examine the stability and repeatability of the prepared nickel reference electrode. The measurements were taken using nickel wire as a working electrode and the prepared nickel reference electrode enclosed within either an alumina or mullite tube. A stainless steel rod (5 mm in diameter) acted as a counter electrode and immersion depth of the working electrode was ~14 mm. The reason for using the prepared reference electrode is to control any issues with the *iR* drop. During measurement, the scan started at an open circuit potential progressing in a negative direction before reversing in a positive direction. Furthermore, cyclic voltammetry was employed to scan and check the nickel working electrode potential stability together with two different types of prepared nickel reference electrodes. Different scan rates were employed during the cyclic voltammetry investigations. The cyclic voltammogram plots are expressed in terms of current rather than current density because the nickel working electrode is used at a fixed depth inside the eutectic molten hydroxide for all cases.

3. Results and discussion

3.1 $Ni/Ni(OH)_2$ reference electrode with an alumina membrane

Cyclic voltammetry (CV) of nickel working electrode in a molten hydroxide (NaOH-KOH, 49–51 mol%) at 300 ^{o}C was carried out. The reference electrode used in the CV study contained a nickel wire inserted inside an alumina tube comprising of a salt mixture ($Ni(OH)_2$-(NaOH-KOH), 1–99 mol%). Fig. 3 shows the CV obtained at a scan rate of 100 mV s^{-1}. The electrochemical stability window is observed for nickel working electrode in eutectic molten hydroxides at 300 ^{o}C is about 0.20 V vs. $Ni/Ni(OH)_2$. In addition, the electrochemical stability window of the nickel electrode in molten NaOH-KOH at 280 ^{o}C is 0.35 V vs. Ag/AgCl [18]. The main reactions of cathodic (C or C') and anodic limits (A1) are expressed as reactions (1) and (2) respectively:

Cathode limit: $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$ (1)

Anodic limit: $2OH^- \rightarrow \frac{1}{2}O_2(g) + H_2O + 2e^-$ (2)

From the CVs in Fig. 3, the cathodic limit (C or C') near -0.5 V is likely due to the reduction of water to generate hydrogen gas as expressed in reaction (1). While the anodic limit (A1) near 1.2 V appears due to the main oxidation reaction in eutectic molten hydroxide (reaction 2) because the molten salt reaction contains an OH^- ion. Moreover, it is confirmed from the literature that there were no complex redox oxides transformations in case of Ni electrode. The mechanism of reactions takes place on anode and cathode in case of Ni electrode is very well explained previously [18]. These results agree with Miles et al. [18], they reported gas evolution at both anodic and cathodic limits. There is a strong possibility that these could be hydrogen and oxygen gases formed from both cathodic and anodic reactions [18]. Furthermore, they stated that the oxidation peak encountered during electrolysis of molten NaOH−KOH at 280 °C using a nickel working electrode was due to the oxidation of NiO to NiO_2 according to the following reaction (3):

$$NiO + 2OH^- \rightarrow NiO_2 + H_2O + 2e^- \quad (3)$$

Consequently, nickel oxide (NiO_2) forms when nickel surface is in touch with the molten hydroxide and peak (A) at 0.46 V (Fig. 3) is attributed to the oxidation of NiO to NiO_2. Furthermore, Miles et al. [18] also found that when a nickel crucible was used for heating LiOH-KOH at 500 °C, it became evenly blackened. Llopis et al. [31] also reported that nickel crucibles containing molten NaOH form a protective black oxide layer. After understanding the main reactions at anodic and cathodic limits, it is imperative to study the change in behaviour of the nickel working electrode during CV tests. Looking at the CVs in Fig. 3, there is a shift in the oxidation potential noted for the formation of NiO_2 at peak A'. The CVs were scanned 5 times; scan 1 to 4 has a similar oxidation potential of 0.42 V while for scan 5, the potential peak has shifted to a more positive potential value of 0.53 V. The shift in the oxidation peak is also accompanied by slight shifts in the cathodic limit potential.

This shift in the oxidation peak is likely due to the fact that the hydroxide ions are unable to penetrate easily through the alumina membrane after a certain amount of time. This then leads to higher ionic resistance, which in turn prevents a stable ionic channel with the internal reference electrolyte mixture. In order to understand the main reactions of nickel working electrode and the behaviour of electrode during the test, an investigation of electrode kinetics at different scan rates was also carried out. The reason for carrying out this investigation was to determine the accuracy of the reference electrode potentials and understand how a change in the scan rate can affect the kinetics of electrolytic process.

Fig. 4 shows cyclic voltammetry results obtained at different scan rates at a temperature of 300 ^{o}C. The change and shift of the NiO_2 oxidation peak (as arrow indicated in Fig. 4) is close to 230 mV and varies from 0.36 to 0.53 V as the scan increases from 50 to 150 mV s^{-1}. The cathodic limit that is assigned to the generation of hydrogen gas also shifts positively from 0.05 to 0.15 V (i.e. a 100 mV increase) as scan rate increases from 50 to 150 mV s^{-1}. The oxidation peak at C, C2 and C3 becomes a complex reaction area. Furthermore, the oxidation reaction of NiO to NiO_2 is an irreversible reaction and there is an increase in the oxidation peak current with an increase in scan rate from 50 to 150 mV s^{-1}. Therefore, these scan rates variations likely indicate poor stability of the reference electrode in eutectic molten hydroxide. The reason for this poor stability is the fact that alumina membrane has a high resistance, making it difficult to build a stable ion channel between electrolyte and internal reference electrolyte mixture with the passage of time. Moreover, the poor stability of alumina membrane means that it did not give reproducible results with time and fluctuation has been noticed in all voltammograms (Fig. 5). These fluctuations are noted with 24 h time, however, this type of fluctuation has not been noticed with mullite membrane (Fig. 9). Moreover, Alumina with Au/Ni electrical contact has shown very limited electrical activity in alkaline solution [32].

In order to further check the stability, reusability and lifetime of the prepared nickel reference electrode covered with an alumina membrane tube. The CV examination was repeated at same operating conditions as in the previous test performed after 24 h (Fig. 3). Fig. 5 shows the cyclic voltammetry of nickel working electrode in eutectic molten hydroxide at 300 ^{o}C using the same nickel reference electrode covered with an alumina membrane tube. From Fig. 5, it is obvious that the oxidation peak of NiO_2 shifts negatively from scan 1 to 5. This shift in the oxidation peak between A and A' is about 280 mV and lies between 0.38 and 0.1 V. Meanwhile, there is also a negative shift for the cathodic limit from scan 1 to 5 as shown in Fig. 5. This shift is about 200 mV and lies between -0.02 and -0.22 V. The current of cathodic limit also decreases from 271.1 mA in scan 1 to 99.4 mA in scan 5. This decrease in the current value between scan 1 and 5 in Fig. 5, likely indicates that there was a decrease in the yield of hydrogen gas during the actual experiment. The possible reason behind these shifts could be the high resistance of the alumina membrane.

Furthermore, the results observed from the cyclic voltammetry test to check the stability and reusability of the nickel reference electrode covered by an alumina membrane tube were compared. Scan 3 from both Fig. 3 and Fig. 5 was merged into one figure to clarify the difference in the reference electrode’s behaviour with time as shown in Fig. 6. Among all performed scans the stable results were observed at scan 3, that is why this scan was selected for comparison. Fig. 6 clearly indicates the unstable behaviour of nickel working electrode in eutectic molten hydroxide during the cyclic voltammetry test. This unstable performance is due to the difficulty exhibited by the prepared nickel reference electrode in terms of controlling the nickel working electrode. Therefore, the nickel reference electrode covered with an alumina membrane tube, in terms of stability is not a desirable option for a reference electrode. The compared scan in Fig. 6 shows that there is a negative shift in the oxidation peak of about 200 mV when Test 1 was repeated after 24 h (Test 2).

In terms of the reusability, the nickel reference electrode covered with an alumina membrane tube was also tested after 36 h at the same operating conditions as in Fig. 5. During cyclic voltammetry study, the open circuit potential was very unstable and hence abnormal CV scans were obtained. Moreover, these unstable CV tests for stability and reusability were repeated three times with unchanged results obtained. The main reason for the poor stability of nickel reference electrode coupled with alumina tube membrane is that the eutectic molten hydroxide cannot permeate through alumina membrane that is made from inert $\propto$-Al_2O_3 with high resistance. Since the mixture does not form a stable ion channel with the internal reference electrode-electrolyte mixture, instability abounds. In addition to this instability, this reference electrode cannot be used for more than two consecutive days to function as a part of a reliable electrochemical test because the alumina membrane ($\propto$-Al_2O_3) becomes very high resistance material in eutectic molten hydroxide. Thus, it can be concluded that the prepared nickel reference electrode covered by an alumina membrane tube has a very short usable lifespan. While in literature this membrane material was exhibited very satisfactory results but at much high temperature for Ag/AgCl electrode [25].

3.2 Ni/Ni(OH)$_2$ reference electrode with a mullite membrane

In order to overcome the shortcomings of an alumina membrane, a commercial mullite membrane was used to fabricate the reference electrode. A mixture (Ni(OH)$_2$-(NaOH-KOH); 1–99 mol%) was used as an internal electrolyte and a nickel wire was inserted into the tube containing the electrolyte mixture. The mullite tube was sintered by ∝-Al$_2$O$_3$ and SiO$_2$. The cyclic voltammetry results are shown in Fig. 7. These CV tests were carried out using a nickel wire as a working electrode and prepared nickel wire covered with mullite membrane tube as a reference electrode in the eutectic molten hydroxide at 300 °C with a scan rate of 75 mV s^{-1}.

The potential of the oxidation peaks for scan 1 to 5 was about -0.068 V. Consequently, the reduction potential of cathodic limit for hydrogen gas formation for all scans is about -0.34 V. These preliminary results obtained using the prepared reference electrode in eutectic molten hydroxide confirms its stability and reliability. Therefore, 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. These observed results in terms of stability due to freshly prepared nickel reference electrode covered by a mullite tube is different from the results obtained from the freshly prepared nickel reference electrode covered by an alumina tube. Therefore, the stability of this reference electrode is confirmed and in accordance with the stability analyses of Fu, Guopeng et al. [33].

In order to understand the behaviour of nickel working electrode during eutectic molten hydroxide reaction, the scan rate for cyclic voltammetry observations was changed from slow to fast. The results obtained by changing the scan rate in cyclic voltammetry between 50 and 150 mV s^{-1} at 300 ^{o}C using a nickel reference electrode covered with a mullite membrane tube are shown in Fig. 8. These results of stability are in accordance with the other reported Ag/AgCl reference electrode [23].

The potential of oxidation peak as shown in Fig. 8 is very stable with an increase in scanning rate from 50 to 150 mV s^{-1}. There is no shift in the potential of oxidation peaks for the formation of NiO_2, however, the value of oxidation potential is close to -0.03 V. These results further authenticate the reliability and stability of the nickel reference electrode covered by the mullite membrane [34]. As mentioned before, this stability and reliability of the 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. Consequently, forming a stable ion channel between the internal electrolyte ($Ni(OH)_2$-(NaOH-KOH)) and external electrolyte of the eutectic molten hydroxide.

In order to check the reusability of the prepared reference electrode in eutectic molten hydroxide, the CV test was repeated after 24 h. Fig. 9 shows the obtained results at temperature of 300 ^{o}C and scan rate of 75 mV s^{-1}. The observed scans show a slight positive shift in the oxidation peak. These results were obtained by reusing the reference electrode after 24 h as shown in Fig. 9. This shift in the scans is about 64 mV between scan 1 and 5, thus it can be considered negligible. Furthermore, the reduction potential also stays the same during the test at -0.34 V. This stable behaviour of nickel reference electrode covered by a mullite tube confirms the ability to reuse it and get reliable results. In contrast, the nickel reference electrode covered by an alumina tube was unstable during the test and shifted negatively by about 280 mV.

The CV scans of a freshly prepared nickel reference electrode covered by mullite membrane tube were compared with the CV scans of the same reference electrode after 24 h at same operating conditions. The reason for comparing these scans is to gauge the durability and stability of the reference electrode that controls the working electrode potential inside the eutectic molten hydroxide during electrochemical analysis.

Fig. 10 shows a comparison between CV scans obtained on both days. The 5th scan is compared from both days. The potential of oxidation peak for NiO_2 on Test 1 is about -0.07 V and on Test 2 is about -0.04 V. This can be considered as equal and shown via an arrow in Fig. 10. Even though there is no change in the potential, however, the current of oxidation peak for forming NiO_2 increases from Test 1 to Test 2. Moreover, the current increases from 121 mA at point A to 190 mA at point A", this is about 68 mA higher for Test 2 after 24 h. These results noted might because of the somewhat good conducting ability of mullite membrane. The increase in the current of the oxidation peak A" is also followed by an increase in the current of the reduction potential. There is, however, no change in the reduction potential assigned to hydrogen gas generation that further demonstrates the stability of the reference electrode. In comparison, it is observed that the ionic conductivity strength of mullite is higher than the alumina [35-37].

Subsequently, it is significant to further test the stability and reusability of the reference electrode in the bulk molten hydroxides. Because of the fast Si dissolution, it was important to determine the stability of the prepared reference electrode with mullite tube membrane. Therefore, to determine the stability and contamination level of the prepared reference electrode, CV tests were carried out for 10 days. Fig. 11 shows photos of the immersed part of the mullite membrane reference electrode in the bulk eutectic molten hydroxide. These photos were taken for the mullite reference electrode after first, third and tenth day of use in the test.

It is obvious from the photo in Fig. 11(a), which was taken for mullite membrane after the first test of the reference electrode, there is no drastic change in the external appearance of the mullite membrane. However, there is a slight corrosion line on the outside surface of the membrane after it was used on the third day as seen in Fig. 11(b); previously this little corrosion is also mentioned by Gao, P., et al., [22]. This change in the reference electrode surface does not affect the stability of the scans. Using the reference electrode to carry out CV studies and hence examining its stability and lifetime was continued until cracks were observed on the tenth day as shown in Fig. 11(c). Therefore, it can be concluded from the above observations that the lifetime use of the reference electrode is at least up to 9 days to avoid any contamination of the outside electrolyte with the internal mixture [22]. The examination of the lifetime of the reference electrode was repeated thrice and it was found that lifetime of the reference electrode was between 7 and 9 days in the chosen eutectic molten hydroxide. Hence, the ideal ionic membrane to construct a reference electrode for eutectic molten hydroxide is mullite because of its stability, reusability and longer lifetime as compared to an alumina membrane. Furthermore, the latter failed to provide a stable ionic channel between the electrolyte and the internal mixture.

4. Conclusions

Comprehensive cyclic voltammetry investigations were carried out to findout a suitable ionic membrane to contain a nickel reference electrode. A mullite membrane that covers Ni/Ni$(OH)_2$ electrode was found to have more stable behaviour in comparison to the alumina membrane for the eutectic molten hydroxide. The findings of this work are summarised as follows:

- The factors that can control the functioning of a reference electrode are temperature, membrane material, internal electrolytic material, scan rate and time.
- The Ni/Ni(OH)$_2$ alumina membrane reference electrode in the eutectic molten hydroxide generated unreliable and inconsistent results. The performed cyclic voltammograms for a freshly prepared reference electrode were unable to produce stable scans, resulted in the scan shifting in a positive direction. Changing the CV scan rate also resulted in significant shifts in the potential of the oxidation peak.
- The Ni/Ni(OH)$_2$ alumina membrane reference electrode was reused after 24 h; a significant negative shift difference (280 mV) in the oxidation peak potential is observed from scan 1 to 5. No CV was produced on the third day, as this was not possible because of the failure of reference electrode.
- The reason for the poor stability of nickel reference electrode covered by an alumina membrane was because of the high resistance of the alumina membrane that leads to issues with creating a stable ion channel between electrolyte and the internal reference electrode mixture (Ni(OH)$_2$-(NaOH-KOH), 1–99 mol%).
- The mullite membrane of Ni/Ni(OH)$_2$ reference electrode was used and tested, only a slight positive shift in the oxidation peak is observed (64 mV from scan 1 to 5). This was considered negligible. The stability of the reference electrode was also tested by changing the scan rate between 50 and 150 mV s^{-1}, the peak potentials were also confirmed to be stable.
- The same mullite reference electrode was reused after 24 h and there was only a small, negligible change in the oxidation peak potential.
- Good mullite membrane reference electrode stability was noted in contrast to the alumina membrane in eutectic molten hydroxide. This is because of the ability of salts to penetrate through and react with the SiO$_2$ that is one of the substances as a part of the structure of mullite

membrane. Conversely, ∝-Al_2O_3 membrane formed a stable ion channel between the internal reference mixture ($Ni(OH)_2$-NaOH-KOH, 1–99 mol%) and the external electrolyte.

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List of Figures

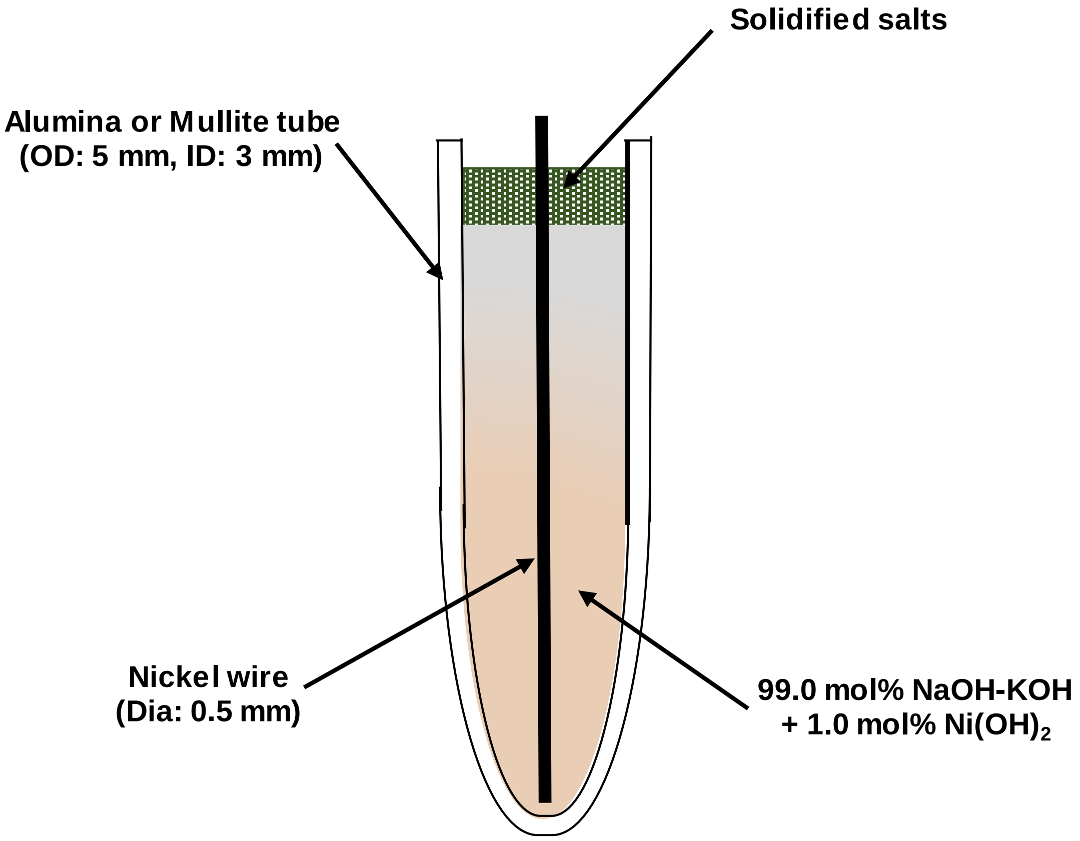


Fig. 1. Assembly of the $Ni/Ni(OH)_2$ reference electrode in a tube membrane.

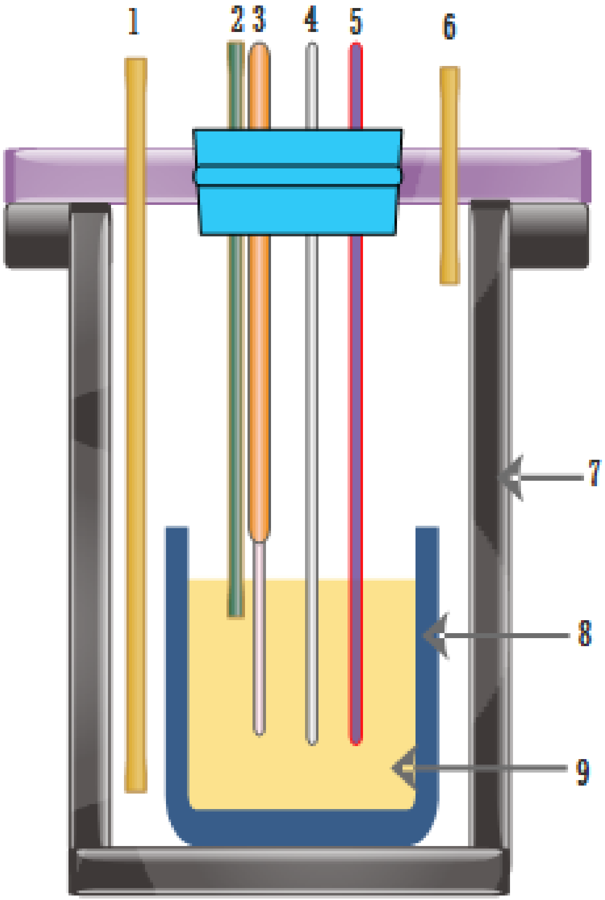


Fig. 2. Schematic diagram of experimental setup: (1) Argon inlet, (2) steam inlet, (3) reference electrode, (4) working electrode, (5) counter electrode, (6) argon outlet, (7), reaction vessel, (8) corundum crucible and (9) molten salt.

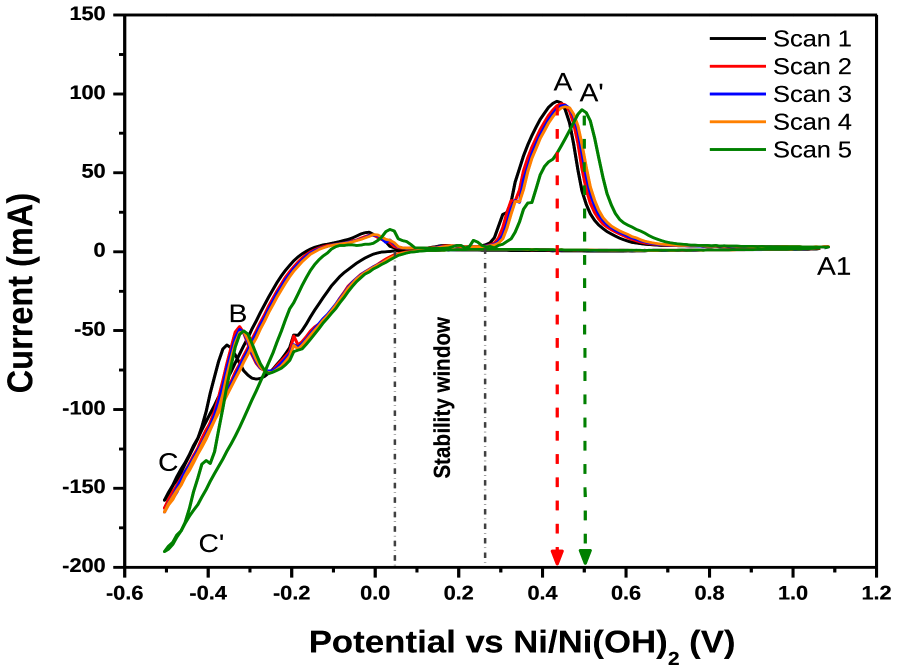


Fig. 3. Cyclic voltammograms of a 0.5 mm Ni wire working electrode (WE) in eutectic molten hydroxide at 100 mV s^{-1} scan rate and scanned negatively from -0.5 to 1.0 V vs. Ni/Ni(OH)$_2$ at 300 °C. Counter electrode (CE): 5 mm diameter stainless steel rod; reference electrode (RE): Ni/Ni(OH)$_2$ in the alumina tube membrane; immersion depth: 14 mm; an Ar gas atmosphere: 40 cm^3 min^{-1}.

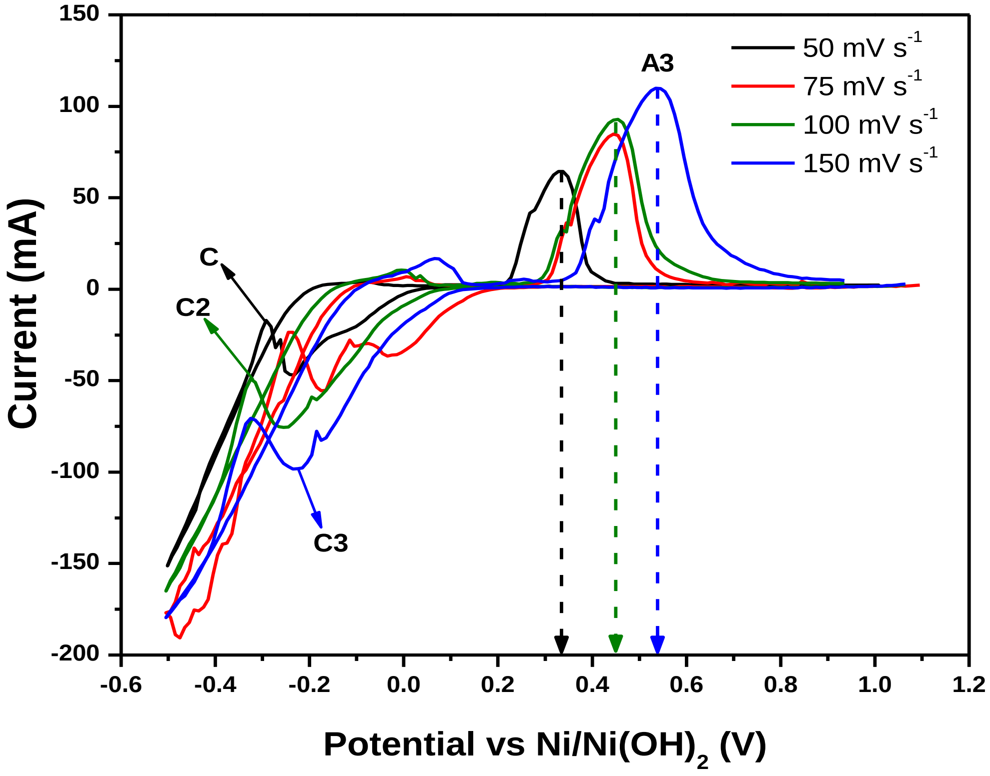


Fig. 4. Cyclic voltammograms of a 0.5 mm nickel wire in eutectic molten hydroxide at different scan rates at 300 °C. RE: Ni/Ni(OH)$_2$ in the alumina tube membrane; CE: 5 mm stainless steel rod; immersion depth: 14 mm; an Ar gas atmosphere 40 cm^3 min^{-1}.

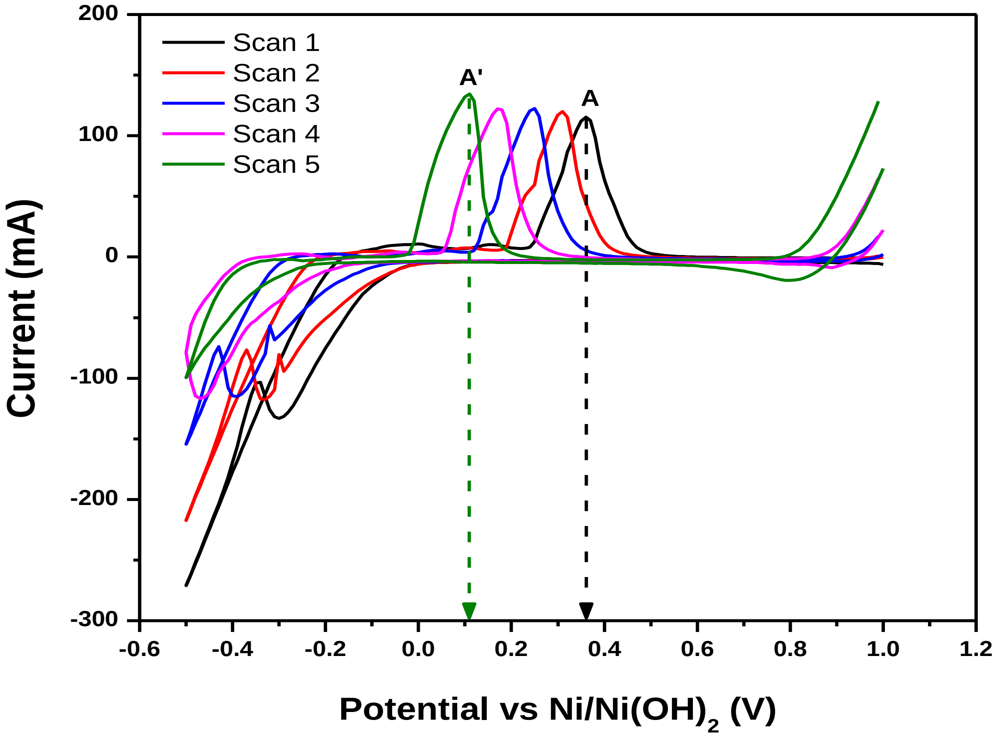


Fig. 5. Cyclic voltammograms of a 0.5 mm Ni wire working electrode in the eutectic molten hydroxide repeated after 24 h (Fig.3**Error! Reference source not found.**). The potential scan negatively from -0.6 to 1.0 V at 300 °C. RE: Ni/Ni(OH)$_2$ in the alumina tube membrane; CE: 5 mm stainless steel rod; immersion depth: 14 mm; an Ar gas atmosphere: 40 cm^3 min^{-1}.

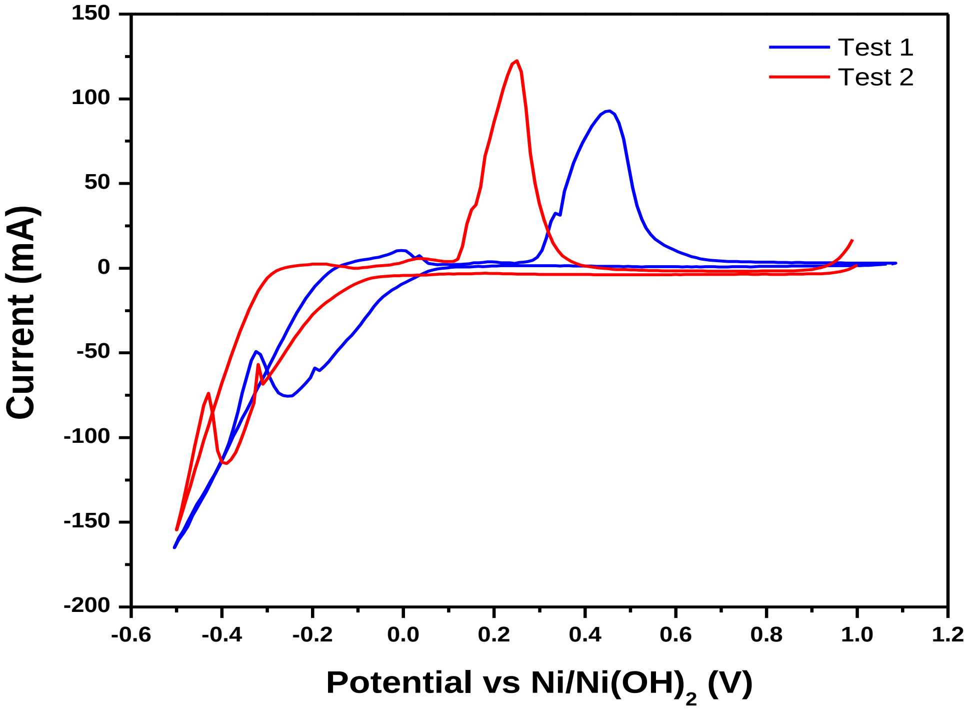


Fig. 6. Cyclic voltammograms of a 0.5 mm nickel wire in eutectic molten hydroxide at 300 °C to compare the reusability of the nickel reference electrode in the alumina tube membrane. CE: 5 mm stainless steel rod; immersion depth: 14 mm; an Ar gas atmosphere: 40 cm^3 min^{-1}.

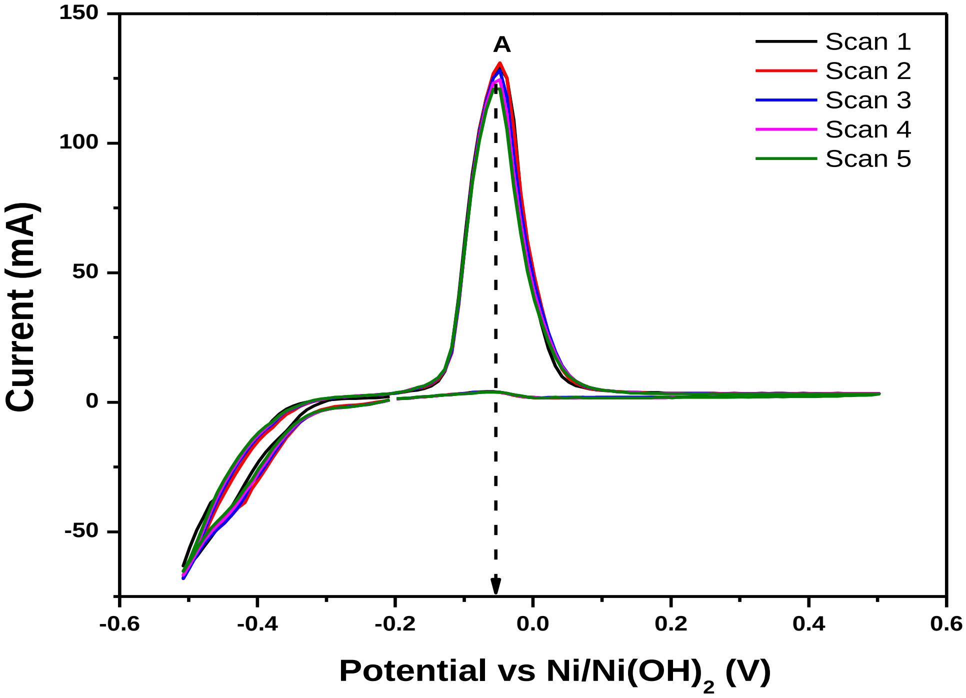
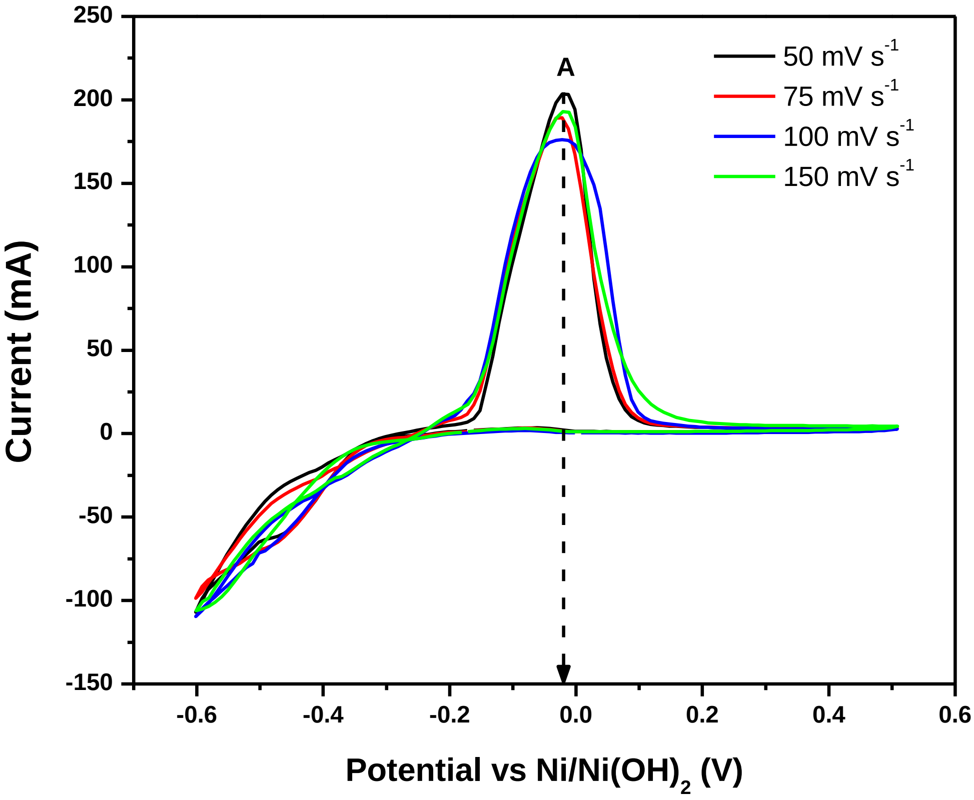


Fig. 7. Cyclic voltammograms of a 0.5 mm Ni wire working electrode in eutectic molten hydroxide; the scan is altered negatively from -0.5 to 1.0 V at 300 °C and 75 mV s^{-1} scan rate; CE: 5 mm diameter stainless steel rod; RE: $Ni/Ni(OH)_2$ in the mullite tube membrane; immersion depth: 14 mm; an Ar gas atmosphere: 40 cm^3 min^{-1}. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



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565 **Fig. 8.** Cyclic voltammograms of a 0.5 mm nickel wire in eutectic molten hydroxide with
566 different scan rates at 300 °C. RE: Ni/Ni(OH)$_2$ in the mullite tube membrane; CE: 5 mm
567 stainless steel rod; immersion depth: 14 mm; an Ar gas atmosphere: 40 cm^3 min^{-1}.
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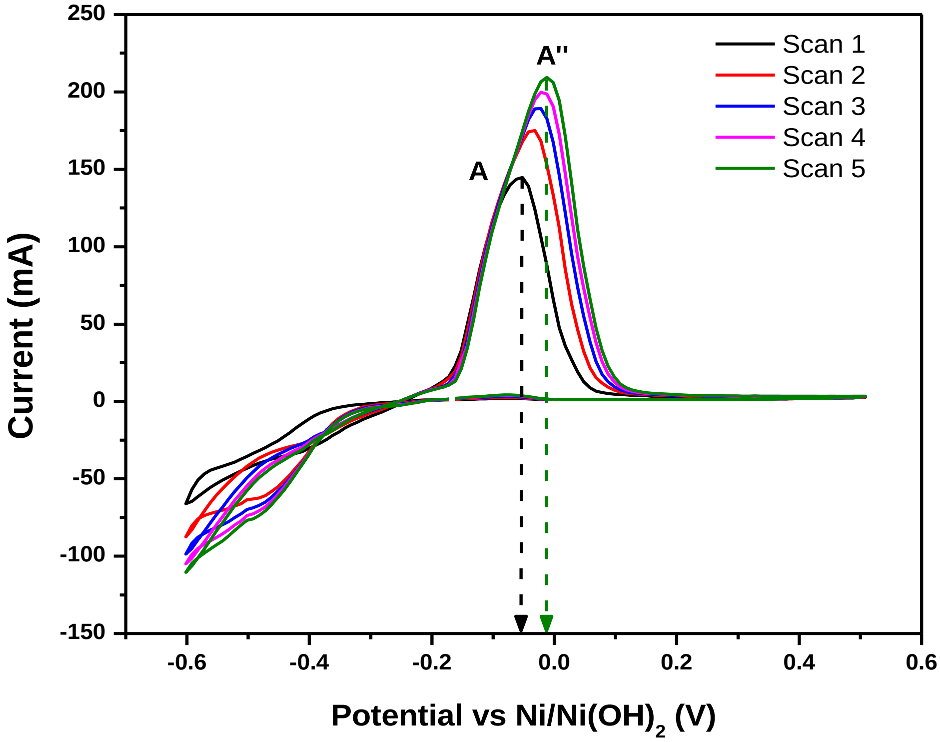

Fig. 9. Cyclic voltammograms of a 0.5 mm Ni wire working electrode in eutectic molten hydroxide repeated after 24 h (Fig. 7). The potential is negatively scanned from -0.6 to 1.0 V at 300 ^{o}C. RE: Ni/Ni(OH)$_2$ in the mullite tube membrane; CE: 5 mm stainless steel rod; immersion depth: 14 mm; an Ar gas atmosphere: 40 cm^3 min^{-1}.

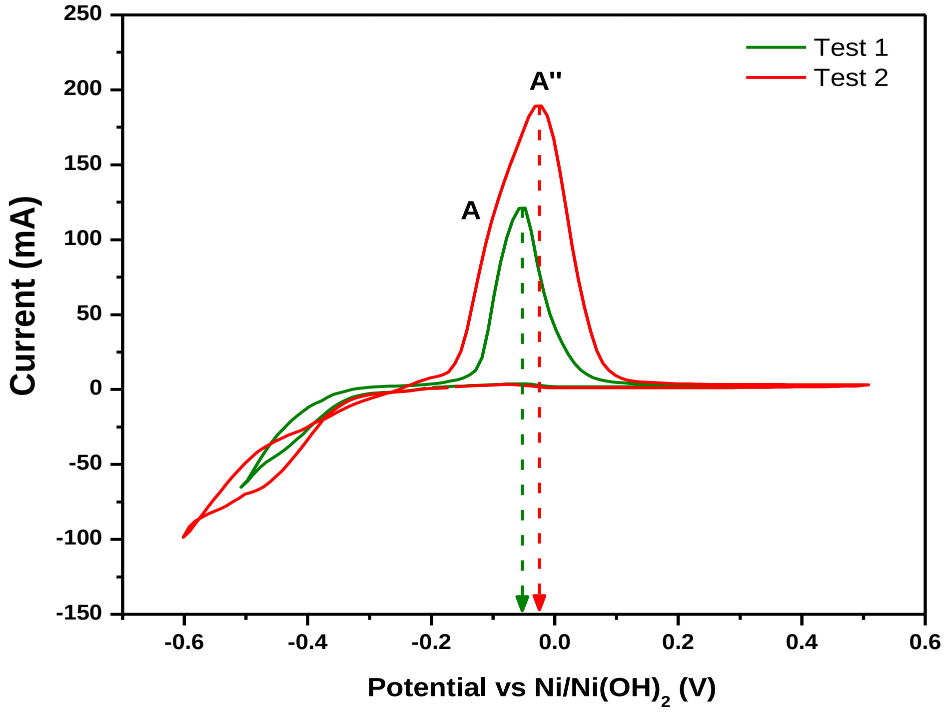

Fig. 10. Comparison of cyclic voltammograms of the repeatable use of the nickel reference electrode in the mullite tube membrane (Fig. 9 and Fig. 7). The 0.5 mm nickel wire in eutectic molten hydroxide at 300 ^{o}C has been used for comparison. CE: 5 mm stainless steel rod; immersion depth: 14 mm; an Ar gas atmosphere: 40 cm^3 min^{-1}.

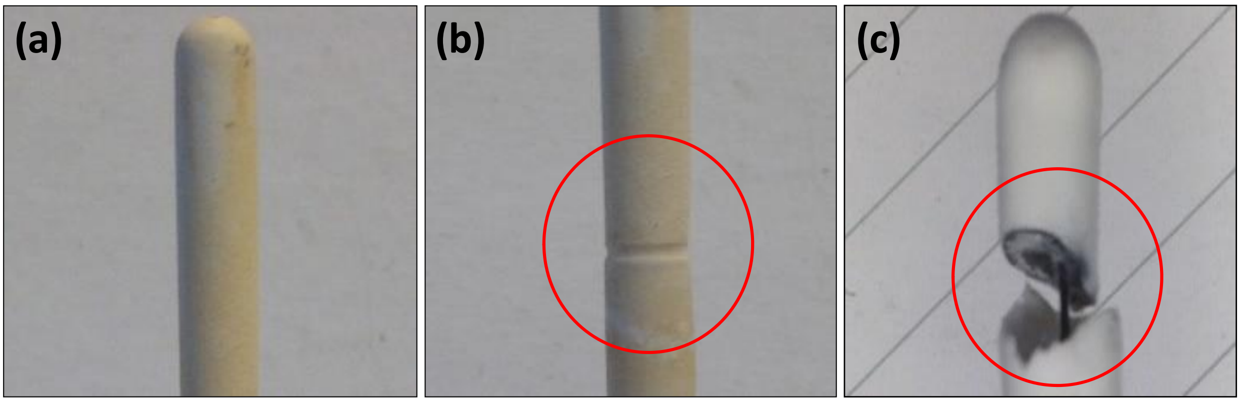

Fig. 11. The change in the nickel reference electrode coupled with a mullite tube membrane inside eutectic molten hydroxide: (a) 1st day, (b) 3rd day and (c) 10th day.

TOC

Description

This study investigates a suitable material for the fabrication of novel reference electrode for hydrogen gas production. The designed nickel reference electrode is successfully examined for reusability and stability by using electrochemical and cyclic voltammetry techniques.

Graphical abstract