Electrolytic Hydrogen Charging of Zr-2.5Nb Alloy in Molten NaOH-KOH Eutectic Mixture at Low Overpotential

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
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Abstract

The major contributions of this thesis include: first, it proved the effectiveness for the method of electrolytic charging Zr-2.5Nb alloy with hydrogen in moist NaOH-KOH melt at low overpotential; second, it employed a Hg/HgO RE in YSZ membrane and investigated its performance; last, it found an optimized voltage range for the potentiostatic charging process. The equilibrium potential of hydrogen evolution reaction in the melt is estimated to be slightly higher than -0.85V, measured by the Hg/HgO RE. The optimized voltage range is -0.85 V to -0.875 V. Within this range, scattered hydride distribution in the internal metal bulk is observed, and hydrides precipitate at controllable rates, avoiding the intensive accumulation in a thin subsurface layer. The Hg/HgO RE provides a stable and reproducible OCP reading around -0.785 V for nickel plated zirconium samples in the melt. The potential difference between the three Hg/HgO RE for this project is ±10 mV.
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1. Introduction: pressure tubes of CANDU reactor

The CANDU reactor, which is the abbreviation of CANada Deuterium Uranium reactor, is a Canadian-developed, pressurized heavy water nuclear reactor. It uses deuterium oxide for moderator and coolant, and natural uranium as fuel [1]. Being the most efficient in terms of uranium consumption, it uses about 15% less uranium than a pressurized water reactor (PWR) for every kilowatt-hour of electricity generated [1]. Due to the usage of natural uranium, the costs of uranium enrichment and reprocessing are eliminated, and the source of fuel supply is widened to accept low-fissile content fuels as well. The most unique advantage of CANDU reactor is the design of its reactor core, which allows on-power refueling and ensures the continuity of the reactor operation [1]. Unlike PWRs and BWRs, which employ one large pressure vessel and batch refueling, the CANDU reactor core consists of 380 horizontal fuel channels connected with a feeding system, to load the fuel assemblies while the reactor is on power [1]. The fuel channels are held in a vessel named calandria, and each of the channels comprises a pressure tube, a calandria tube, end fittings, and garter springs. Having direct contact with the fuel bundles and heavy water, the pressure tube experiences severe working conditions and its durability has become the focus of many researches. This work covers the embrittlement issue of the pressure tubes and develops a method to reproduce the embrittlement process under non-irradiated conditions using electrochemical techniques, for exploring the service limits of these tubes.
2. Overview of pressure tube embrittlement

2.1 Pressure tube design

The pressure tubes are made of Zr-2.5Nb alloy, which has its composition listed in Table 2.1. The tubes are designed to hold the fuel bundles and regulate the heavy water flow inside. They are connected with the heat transport system through 403 stainless steel end fittings [2]. A thin calandria tube made of Zircaloy-2 alloy holds the pressure tube inside and leaves a gap between them. This gap is called the annulus gap and filled with dry CO₂ gas, providing insulation between the tubes. The dry CO₂ is also an effective way to detect cracks of pressure tube and leakage of the D₂O, since the CO₂ moisture content would change when the leakage happened. To prevent direct contact between the pressure and calandria tubes, garter springs are installed in the annulus gap [3]. Fig 2.1 provides a general schematic of the pressure tube design. For the latest Enhanced CANDU 6 reactor (EC6), the reactor inlet header operating temperature and pressure are 265 °C and about 11 MPa, and the outlet operating temperature and pressure are 310 °C and 9.89 MPa [4, 5].

The failure of pressure tubes was first reported in 1974 at Pickering unit 3, which led to a reactor shut down for 230 days [2]. The pressure tube and calandria tube contacted with each other and led to significant thermal gradients and deuterium migration. Heavy water was found leaking into the annulus gap [6]. Seventeen cracked pressure tubes were identified and replaced. Similar failures were reported by other sites soon after [7]. A detailed list of pressure tube failures is included in Appendix A [2]. The reason for these failures was found to be the Delayed Hydride Cracking (DHC) phenomenon, which is discussed in the next section.
Table 2.1: Composition of the double melted Zr-2.5Nb alloy pressure tubes [8].

<table>
<thead>
<tr>
<th>Nb % (wt)</th>
<th>O (ppm)</th>
<th>C (ppm)</th>
<th>Fe (ppm)</th>
<th>H (ppm)</th>
<th>N (ppm)</th>
<th>Cr (ppm)</th>
<th>Zr + other impurities</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4-2.8</td>
<td>900-1300</td>
<td>125</td>
<td>&lt;1500</td>
<td>&lt;25</td>
<td>&lt;65</td>
<td>&lt;200</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Fig 2.1: A general schematic of the pressure tube design [9].
2.2 Hydride formation and DHC

The hydrogen contents in the heavy water coolant originate from various sources. Some of the external ones which add hydrogen to the coolant can be waterside corrosion, stainless steel corrosion, dissolved hydrogen in the coolant, and water radiolysis. Internal ones such as hydrogen contents and moisture absorbed in fuel pellets are also significant sources of hydrogen [10]. Among all the sources above, the direct reaction of the pressure tube and heavy water is considered to be the main contributor. The tube surface adsorbs these hydrogen contents, forming adsorbed hydrogen species according to the following equations [11]:

\[ \text{H}^0 + \text{Zr} \rightarrow \text{Zr-H}_{\text{ads}} \]  \hspace{1cm} (1)  

\[ \text{H}^+ + \text{e}^- + \text{Zr} \rightarrow \text{Zr-H}_{\text{ads}} \]  \hspace{1cm} (2)  

The adsorbed hydrogen species (\text{Zr-H}_{\text{ads}}), undergo a interfacial hydrogen transfer process, which turns the hydrogen from adsorbed to absorbed state [11, 12]:

\[ \text{Zr-H}_{\text{ads}} \rightarrow \text{Zr-H}_{\text{abs}} \]  \hspace{1cm} (3)  

The absorbed hydrogen contents then diffuse in the metal bulk. Zirconium and its alloys have a limited solid solubility for hydrogen, therefore, when the absorbed hydrogen contents exceed the terminal solid solubility (TSS), the hydrogen will precipitates out as hydrides in the matrix [13, 14]. Although at elevated temperature, such as 500°C, zirconium alloys have hydrogen solubility as high as 450 ppm, this value steeply decreases to 65 ppm when the temperature drops to 300°C. At room temperature, the solubility could be extremely low as 0.05 ppm [15, 16]. Having weaker mechanical toughness, the accumulated hydrides can cause the embrittlement of the zirconium alloy, leading to a reduction in ductility, impact and fracture toughness. For a significant reduction in these mechanical properties, a certain volume fraction of hydrides is required and the degree of the embrittlement also depends on the orientation of the hydrides [15].
The hydrogen contents in the pressure tube tend to migrate to areas with high local stress, such as discontinuous sites and small flaws, where the stress intensity factors are high [17]. As a result, local hydride volume fractions will increase gradually in these areas. Subsequently, hydride blisters will form and drastically reduce the mechanical properties of the tube, which may lead to cracking [7, 17]. This process is called **Delayed Hydride Cracking (DHC)** [18]. Excessive residual stresses at the roller joint position caused by an improperly rolled joint are found to be one of the main causes for the DHC [19]. Due to the excessive residual stress, hydride volume fractions at the coolant inlet position become high. As more hydrogen contents get picked up by the pressure tube during normal operation, the number and size of blisters continuously increase, leading to a critical defect eventually [20].

Generally, three essential factors are required to initiate DHC: stress, hydrogen, and time. If one of them is missing, the DHC phenomenon may not happen.
2.3 Methods of hydride formation in the laboratory

There are generally three ways to precipitate hydrides in zirconium alloys in the laboratory. Each of them requires different reaction conditions and employs different interaction between the hydrogen and metal matrix [21]. The first method is called physisorption [22]. Having the lowest reaction temperature from 5 to 20K, physisorption is considered to be the least feasible and efficient for hydride precipitation due to lack of dissociated hydrogen. At this extremely low temperature, when hydrogen molecules contact with the metal surface, small Van der Waals interaction force adheres the hydrogen molecules on the metal surface [23]. The reaction can be expressed by:

\[
H_2 + Zr \rightarrow Zr-H_{2(phy)}
\] (4)

The binding energy of the \(Zr-H_{2(phy)}\) bond is between 3.5 to 15 kJ\(\cdot\)mol\(^{-1}\). With this low binding energy, this bond is easy to break when the temperature increases [24].

The second method is named chemisorption. Unlike physisorption at low temperature, chemisorption employs hydrogen-metal contact at higher temperature. Experiments have shown that this temperature can be as low as 300K [25]. The hydrogen molecules first approach the metal. Before interacting with the surface, they dissociate into hydrogen atoms with aid of the surface’s chemisorption energy, which exceeds the dissociation energy of hydrogen molecules [26, 27]. It is considered that the metal surface functions as a catalyst for the dissociation of hydrogen. The free and energetically rich hydrogen atoms then form chemical bonds with the metal surface. The reactions can be expressed by [21, 28]:

\[
H_2(\text{Surf}) \rightarrow 2H^*(\text{Surf})
\] (5)

\[
H^*(\text{Surf}) + Zr \rightarrow Zr-H_{\text{chem}}
\] (6)
The bond energy of Zr-H\textsubscript{chem} is about 250 to 270 kJ\textbullet{}mol\textsuperscript{-1}. After the formation of the chemical bond, the heat of adsorption will be released. The hydrogen atoms adsorbed on the surface by this bond subsequently dive into an interstice below the first metal surface monolayer and diffuse into the metal bulk, becoming absorbed hydrogen [29].

The last method is called electrodosorption. Unlike the previous two methods, electrodosorption does not employ gaseous hydrogen as source of hydrides. Instead, aqueous electrolytes containing protons or water molecules are used to provide the hydrogen [30]. In aqueous solution, proton can not exist by itself and is bonded with a water molecule, which has a non-bonding electron pair and functions as an electron donor. The H\textsubscript{2}O\textsuperscript{+} formed will further bond with another three water molecules, creating the time-average state H\textsubscript{9}O\textsubscript{4}\textsuperscript{+} [21]. The H\textsubscript{9}O\textsubscript{4}\textsuperscript{+} ions can also be written as H\textsuperscript{+} \cdot 4H\textsubscript{2}O. With an external electrostatic field applied over the electrolyte, the H\textsuperscript{+} \cdot 4H\textsubscript{2}O ions will be transported to the cathode and contact with the metal surface, where the protons get discharged and adsorbed by the metal surface [31]. The reaction can be described as:

\[
\text{H}^+ \cdot 4\text{H}_2\text{O} + e^- + \text{Zr} \rightarrow \text{Zr-H}\textsubscript{ads} + 4\text{H}_2\text{O}
\]  

(7)

The hydration shell surrounding the proton is dismantled after the proton is adsorbed on the metal surface [21, 31]. Similar to chemisorption, the adsorbed hydrogen will be absorbed by the metal bulk and diffuse into deeper subsurface, which can be expressed as:

\[
\text{ZrH}\textsubscript{ads} \rightarrow \text{Zr-H}\textsubscript{abs}
\]

(8)

The hydriding method used in this work belongs to electrodosorption, but instead of having aqueous solution, a molten alkali mixture containing water is used as the electrolyte and hydrogen provider. The reason for choosing this mixture of NaOH and KOH at the eutectic point will be discussed in Section 2.5.

There are several common points between the chemisorption and electrodosorption methods of hydriding. One is that their rate limiting steps are both the diffusion of absorbed hydrogen in the
metal bulk [21]. Therefore, after hydriding, the cross-sectional images for samples using the two methods both show up a layer of hydrides accumulated beneath the surface [21]. In order to distribute these accumulated hydrides evenly through the entire sample, researchers are currently using annealing at higher temperature for extended period of time [32]. But the annealing is suspected to change the atom displacement of the actual samples from reactors since the annealing temperature is often higher than the hydriding temperature. The hypothesis that low hydriding rate and high temperature may eliminate the accumulated hydride layer and spread the hydrides evenly in the sample exists, and it is also one target of this work to test this hypothesis.
2.4 Review on previous studies of hydriding

The characteristics of zirconium hydrides, such as solubility, morphology, and orientation, have been studied by many research groups. This section summarizes two outstanding studies as typical cases and discusses some of the major discoveries that have been made.

Singh et al studied the influence of hydrogen contents on the impact toughness of Zr-2.5Nb pressure tube alloy [32]. They used the chemisorption method to charge the double melted and unirradiated samples to target hydrogen concentrations of 20, 60, 80, and 150 wppm. The samples were charged in hydrogen gas at 363°C and the charging duration was no more than 1 hour. An annealing period of 24 hours at 400°C was then applied to obtain a uniform hydride distribution. After the annealing, an instrumented drop weight impact testing machine was used to generate the load displacement plot. The results show that the hydride platelets oriented along the axial direction are straighter and longer than those oriented along the circumferential plane. Fig 2.2 shows a comparison of the hydrides observed in the axial and circumferential directions from Singh. In these images, the dark lines represent the traces of hydrides. In addition, no hydride platelets were oriented in the radial direction. Singh believes that this phenomenon is attributed to the microstructure of the tube. The microstructure consists of two phases: an α-Zr grain phase which is strongly textured and heavily elongated in axial direction, and a network of β-Zr phase which is very thin and nearly continuous along the grain boundaries. In terms of impact toughness, at room temperature, severe reduction in impact toughness was observed when hydrogen concentration increased over 25 ppm. Fig 2.3 shows their results for the impact toughness and energy-to-fracture measurement. At 200°C, the impact toughness was also found to decrease drastically before the hydrogen concentration increased to 90 ppm.
Fig 2.2: The microstructure of Zr-2.5Nb pressure tube alloy containing 25, 70 and 170 wppm of hydrogen, revealing traces of hydrides on AR and RC planes, observed by Singh et al [32].
Fig 2.3: Impact toughness and energy to fracture measured by Singh et al [32].
Liu et al investigated the morphology, size and distribution of hydrides generated through cathodic hydrogen charging in an acidic solution, which can be categorized into the electroadsorption method [10]. The sample analyzed was a Zn-Sn-Nb sheet, which was electron beam melted in vacuum, hot and cold rolled, and annealed for 2 hours at 580°C before the hydriding. The hydrogen charging was performed in sulfuric acid of 1N at room temperature, with a constant current density of 0.08A cm$^{-2}$ for 4 hours. The sample was then annealed at 400°C for 6 hours. The results show that the hydride platelets tended to precipitate along the circumferential and the axial direction of the sheet. The size of the platelets was found to be dependent on the cooling rate after the annealing. In naturally cooled sheets, the hydride platelets were distributed more homogeneously. In furnace-cooled sheets, the platelets tended to group into long bands, and had a low nucleation rate at high temperature. The hydrides were identified as δ-ZrH$_2$ by X-ray diffraction and TEM.

However, this cathodic hydrogen charging method using acidic solution has its own limitation, which is the aqueous solution at room temperature. The ideal temperature for charging zirconium materials would be the same as the operating temperature of the pressure tubes. As a result, it is prompted to use an electrolyte that can be heated up to 300°C. Thus, the idea of using eutectic NaOH-KOH melt for the electrolyte is promoted, which is discussed in the next section.
2.5 Electrolyte as molten alkali mixture

As mentioned in the previous section, this project uses a eutectic mixture of NaOH and KOH as electrolyte. There are several reasons for choosing this mixture. First, at eutectic point, the mixture of NaOH and KOH can easily melt at 170°C at atmosphere pressure [33]. Due to its wide liquid range from 170 to 800°C, the mixture can be used at 300°C, which is the operating temperature of the pressure tubes in the reactor core [34]. This avoids the employment of autoclaves and reduces the level of difficulty for the assembly and operation of apparatus. Second, in the liquid phase, the NaOH-KOH melt can still hold an abundant amount of water molecules, which provide the hydrogen required for the hydride formation [35]. In addition, similar to molten salts, molten alkalis have high ionic conductivity, thus reducing the resistance of the electrolyte [36]. The width of the electrochemical window for the NaOH-KOH melt is 1.5 to 2.5 V, which is suitable for many complex electrochemical operations [33, 37].

It has been proven that water in the molten alkali mixture functions as an electroactive specie and the limiting current density is direct proportional to the water concentration in the melt. According to the Henry’s Law, at equilibrium, the water concentration in the melt is directly proportional to the partial pressure of water vapour above the melt. Once the equilibrium is broken, the water-rich phase, either as the melt or the gaseous mixture above the melt, will have to transfer part of its water content to the other phase to rebuild the equilibrium. In the author’s experiment, it is found that once the melt was open to air, it quickly lost its water content and steam was observed on top of the melt. Thus to maintain the moisture of the NaOH-KOH melt, a humid environment must be provided, which was achieved by continuous purging of wet nitrogen gas in the author’s experiment. Details of the purging are described in Section 4.1. The wet nitrogen gas is assumed to reach an equilibrium of water with the melt and make up the water consumption during the electrolytic charging.
2.6 Feasibility test using galvanostatic charging

The study of hydriding Zr-2.5Nb material in NaOH-KOH eutectic melt started with a feasibility test done by Dr. Anatolie Carcea in the author’s group. Carcea successfully charged the material and achieved high hydride volume fractions [39]. Fig 2.4 shows an SEM of the polished cross-section of a hydrogen-charged sample generated in the feasibility test. The black lines in the picture represent hydrides.

![Fig 2.4: Internal hydriding of 1 mm thick nickel-plated Zr-2.5Nb after charging at 100 mA•cm⁻², 48 minutes, 300°C.](image)

A three-electrode cell and a potentiostat were used to record the current-potential curves. The hydrogen charging was done using a DC power supply with either constant current density or periodic current pulsing. To precisely control the hydriding process, Carcea found that the melt needs to be isolated from oxygen. Fig 2.5 shows the potentiodynamic polarization of Pt and Zr in the melt open to air at 250°C. The horizontal region in the curve ranging from -1.3 V to -0.3 V is
caused by the oxygen reduction, which provides a limiting current density up to 6 mA cm\(^{-2}\) and masks the hydrogen evolution and absorption data.

**Fig 2.5:** Potentiodynamic polarization of Pt and Zr in NaOH-KOH melt, open to air, at 250°C; scan rate 5 mV s\(^{-1}\).

The current density difference between the Pt and Zr electrodes in Fig 2.5 is probably due to the different geometry of the electrodes: Pt as wire and Zr as foil. In Fig 2.6, when the melt was deoxygenated, the oxygen reduction current density decreased substantially, compared with Fig 2.5. The limiting current density for the horizontal oxygen reduction region drastically dropped to about 0.6 mA cm\(^{-2}\) in Fig 2.6. Thus, it is necessary to eliminate the presence of oxygen in the
melt as much as possible. The experimental apparatus was later transferred into a sealed reaction chamber, which was deaerated before and during the hydrogen charging with wet nitrogen gas.

**Fig 2.6**: Potentiodynamic polarization of two Pt WE in NaOH-KOH melt, both deoxygenated with wet nitrogen at 250°C; scan rate 5 mV•s⁻¹.

In addition, Carcea found that a layer of Ni coating on the sample surface enhanced the hydrogen entry to the metal bulk and could serve as a catalyst for the hydride precipitation. However, the Ni coating corroded when the current density was reduced to lower the reaction rate. Fig 2.7 shows the potential behaviour of nickel-plated Zr-2.5Nb during galvanostatic charging at 1.6 mA•cm⁻². It can be seen that when the current density decreased from 3 to 1.6 mA•cm⁻², the potential quickly increased from -0.88 V to about -0.05 V, which was even higher than the open circuit potential (OCP) at about -0.75 V. This process took only a few minutes to happen. After a
number of cycles of pulsing between high and low current density, which took about 30 minutes, the nickel coating appeared to change colour and peel off from the sample. The OCP measured after the cycles shifted about 0.6 V up. This is probably due to some unknown oxidation reactions happening on the Ni coating. It is concluded that it is not feasible to achieve low hydriding rate using current density adjustment, since at low current density, the potential rises into a region where unknown oxidation reactions take place on the surface and interfere with the hydrogen evolution. Thus the feasibility test suggests to control the hydriding rate through adjustment of potential applied on the sample to avoid this problem. By controlling the potential, the sample can be kept away from the oxidation region, saving the nickel coating on the surface.

![Graph](image)

**Fig 2.7:** Potential behaviour of nickel-plated Zr-2.5Nb during galvanostatic charging at 1.6 mA·cm⁻², in NaOH-KOH melt at 300°C.
2.7 Reference electrodes for molten alkali mixture

Another difficulty encountered during the feasibility study was the lack of a suitable reference electrode for the NaOH-KOH melt. Due to the high operating temperature and extreme causticity of the melt, conventional reference electrodes designed for aqueous systems, such as saturated calomel electrode or silver-silver chloride electrode, cannot be used in this experiment. For potential measurement at high temperature, researchers have developed several pseudo reference electrodes, which can only be used with limited conditions [40]. Pseudo reference electrodes such as Pt and Ag wire were selected and tested in the previous feasibility test by Carcea. The main problem of using the Pt wire is that the electrode surface gets easily contaminated by other metal ions, such as Ni$^{2+}$, in the molten alkali. The Ni$^{2+}$ ions and other impurities deposited on the Pt surface and shifted the potential during measurements. Ag wire was found to dissolve in the melt, which introduced an extra impurity. In addition, the reaction between Ag and oxygen on the electrode surface shifted the potential reading of the electrode. As a result, the design and investigation of a suitable reference electrode in NaOH-KOH melt become an important aspect of this project.

Electrodes using YSZ membrane have been studied in the past few decades for precise pH measurement and potential measurement at high temperature. The YSZ material itself is a zirconium oxide (ZrO$_2$) based ceramic [41]. In the sintering process of manufacturing, some of the Zr$^{4+}$ ions in the zirconia lattice are substituted by Y$^{3+}$ ions for stabilization purpose. Without the substitution, the zirconium oxide suffers from disruptive phase changes when its crystal structure alters with temperature, which leads to weak thermal and mechanical properties. After being doped with yttria, the zirconia lattice becomes more stable and tolerant to temperature change, and obtains oxygen vacancies in its structure [42]. At high temperature, when the vacancy sites turn mobile enough, YSZ becomes capable of conducting O$^{2-}$ ions. The flow of O$^{2-}$ ions in the material thus leads to a current [43]. The ionic conductivity of YSZ is related to temperature and the amount of yttria added in manufacture [44]. With an yttria concentration of
8 mol%, the YSZ material is found to have the largest ionic conductivity around 0.1 S cm\(^{-1}\) at 1000\(^\circ\)C [45, 46].

A Hg/HgO electrode, which has a shell of yttria-stabilized zirconia (YSZ) membrane, is selected as the reference electrode for the author’s experiment. The working mechanism of the Hg/HgO RE is described by the potential determining equilibria on both sides of the membrane listed below [47]:

On the NaOH-KOH melt side:

\[
V_O + H_2O \rightleftharpoons O_O + 2H^+ \quad (9)
\]

On the internal electrode element side:

\[
HgO + V_O + 2e^- \rightleftharpoons Hg + O_O \quad (10)
\]

with \(V_O\) representing one available vacancy site for the \(O^{2-}\) ions, \(O_O\) being one \(O^{2-}\) ion occupying this vacancy and diffusing in the YSZ membrane. On the NaOH-KOH melt side, water molecules contact with the YSZ membrane and dissociate, releasing \(H^+\) and \(O^{2-}\) ions. The \(O^{2-}\) ions then occupy the vacancy sites in the YSZ and transfer through the membrane, reaching the internal electrode element side [48]. The free Hg atoms inside the YSZ tube react with the transferred \(O^{2-}\) ions, forming HgO. The overall equilibrium obtained by summing the two reactions is listed below:

\[
HgO + 2H^+ + 2e^- \rightleftharpoons Hg + H_2O \quad (11)
\]

According to the Nernst equation, the potential of this reaction is determined by [49, 50, 51]:

\[
E = E_{Hg/HgO}^0 - \left(\frac{2.303RT}{2F}\right) \log(a_{H_2O}) - \left(\frac{2.303RT}{2F}\right) \rho H \quad (12)
\]
with $E_{\text{Hg/HgO}}^0$ being the standard potential of the Hg/HgO equilibrium, $a_{\text{H}_2\text{O}}$ being the activity of water molecules in NaOH-KOH melt.

3. Objective

In order to explore the service limit and extend the lifespan of the pressure tubes used in the CANDU reactor, studies on the end-of-life performance of Zr-2.5Nb material are being carried out in several laboratories. As a result, techniques generating tube samples with required hydrogen concentrations are required. So far, methods including gaseous hydrogen chemisorption at elevated temperature and aqueous solution electroadsorption at low temperature are developed, but both of them largely deviate from the actual hydriding conditions in the reactor core. According to the literature review, few studies have considered the possibility of using eutectic NaOH-KOH melt for hydrogen charging Zr-2.5Nb material. The melt contains electrolyzable water at high temperature and could serve as a hydrogen source for the hydride precipitation.

A previous feasibility study has shown that it is possible to charge Zr-2.5Nb samples with hydrogen in moist NaOH-KOH melt. But the control mechanism using current density adjustment appears to be insufficient. In order to generate samples with required hydrogen concentrations, precise potential control with low hydriding rates is required. This work investigates the feasibility of hydrogen charging and controlling the hydriding rate by applying a low overpotential on samples. In addition, the development of a suitable reference electrode for potential measurement in the NaOH-KOH melt is another important aspect of this project.
4. Experimental

4.1 Preparation of eutectic NaOH-KOH melt

For one single batch, the eutectic mixture of NaOH and KOH melt has a total weight of 200 g. The molar ratio of pure NaOH to KOH in the mixture is 51:49. The NaOH pellets used for the mixture are 97 % pure by weight, with the remaining 3 % as water. The KOH pellets used are 85 % pure by weight, with balance as water. Both pellets are products of Alfa Aesar. To produce a mixture of 200 g, 79.5 g of NaOH and 122.5 g of KOH were weighed separately and mixed in a nickel beaker. The beaker was placed in a sealed chamber, which was purged with wet nitrogen gas. The wet nitrogen was produced by passing nitrogen through deionized water. This continuous purging started 30 minutes before the heating process, and stopped when the NaOH-KOH melt reached room temperature again. One band heater held the bottom of the beaker and provided the heat required for the melting. The band heater was controlled by a thermal controller, which adjusted the heating process according to the temperature measured by a thermocouple placed between the band heater and beaker. The difference between the measurement of the thermocouple and the actual temperature of the melt was calibrated in the setting of the thermo controller. It is found that at steady state, the thermo controller needs to be set to 328°C, to obtain an actual melt temperature of 300°C.

The melting process was done in two phases. In the first phase, the mixture experienced its first melting at 300°C for two hours to ensure that all hydroxide pellets were melted. The NaOH-KOH melt appears to be a clear, transparent, and uniform liquid. In the second phase, the band heater was turned off and the melt was cooled down naturally to room temperature. The cooling process took about two hours to complete and the melt turned back to solid again. Twenty four hours later, the solid mixture was melted again using the same procedures. But this time, the melting process took less than 30 minutes. It is found that the NaOH-KOH melt after re-melting contains more water content than the one melted only once. It is presumed that the melt may lose
part of its moisture to the surroundings due to the relatively long period of heating in the first phase. But in the second phase, during the re-crystallization process, the melt recovered its lost by absorbing moisture from the surroundings and stored these water molecules in the solid crystals. Since the purging did not stop until the melt cooled down to room temperature, a significant amount of moisture could be introduced to the reaction chamber and eventually absorbed by the melt. Although the exact composition after the re-melting remains unknown, the NaOH-KOH melt is considered to reach equilibrium with the wet nitrogen gas. All batches of NaOH-KOH melt were prepared using this procedure. Thus, it is considered that the water concentrations for all batches are identical.

In the cyclic polarization and potentiostatic charging process, the melt was also maintained at 300°C. The reason for keeping the melt at this temperature throughout the experiment is that, 300°C is the normal operating temperature of the pressure tubes and the highest temperature allowed for the actual pressure tubes from the reactor without introducing further radiation damages. The actual pressure tubes from the reactor suffer from neutron bombarding during the service, which creates atom displacement in the metal. The atom displacement would be changed during the hydrogen charging when the charging temperature was higher than 300°C, affecting the mechanical properties of the samples. Thus, to eliminate the effect of radiation damage, samples are charged at 300°C constantly throughout this project.
4.2 Sample preparation

The Zr-2.5Nb samples used in the experiment were provided by Kinectrics Inc. The samples were in the form of slices cut from a miniature pressure tube, with dimensions of 10 mm (circumferential) x 30 mm (axial) x 1 mm (radial). They were cut in half for testing. A Zr wire (99.99 % purity) was spot-welded for connection purposes. The total surface area of one sample is about 3.77 cm$^2$. Before hydriding, the sample was plated with a nickel layer to improve the hydrogen entry.

The Ni plating was completed in two steps. The sample was first immersed in an activation solution for 3 minutes to completely remove the surface oxide layer. The activation solution contains 0.515 g NH$_4$FHF and 0.105 g H$_2$SO$_4$, with a total volume of 100 mL. During the activation, the sample rapidly lost its shiny metal surface and turned into a matt black color, with formation of a large amount of bubbles. After 3 minutes in the activation solution, the sample was quickly pulled out and transferred to the nickel plating solution, which contained 6.5 g NiSO$_4$·6H$_2$O, 2.25 g NiCl$_2$·6H$_2$O, and 4.25 g H$_3$BO$_3$ with a total volume of 100 mL. The transfer needs to be done within 2 seconds to avoid the re-oxidation of the surface. The next step is the nickel plating on the surface, with assistance of a potentiostat. The working electrode terminal of the potentiostat was connected to the sample and the counter electrode terminal was attached to a carbon rod, which was also immersed in the nickel plating solution. The plating current density was set to be -50 mA cm$^{-2}$, thus the total current was about -189 mA, which was the product of the current density and sample surface area. The plating time was set to be 270 seconds. Both the activation solution and nickel plating solution were kept at 60$^\circ$C during the operation. The sample surface turned light grey after the plating. The thickness of the nickel layer coated was about 4 to 5 µm.
4.3 Hg/HgO Reference electrode construction

The YSZ membranes used in the experiment are manufactured by CoorsTek, and contain 9 % yttria in weight, which gives a mole percentage about 5 %. Other components of the material are listed in Table 4.1.

Table 4.1: Composition of the YSZ membrane used [52].

<table>
<thead>
<tr>
<th>Components</th>
<th>ZrO₂+HfO₂</th>
<th>Y₂O₃</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight%</td>
<td>87.6</td>
<td>9</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.4</td>
</tr>
</tbody>
</table>

The membranes are fully stabilized, with a dimension of OD 0.25 inch, ID 0.188 inch and length 11 inches. One end of the tube is closed while the other end remains open.

The electrode element of the Hg/HgO reference electrode (Hg/HgO RE) is a mixture of Hg and HgO. Fig 4.1 shows the structure of the Hg/HgO RE. The Hg and HgO were first mixed in a crucible with a volume ratio about 1:1 and then transferred to the bottom of the YSZ tube. The electrical connection to the Hg/HgO mixture was done by a measuring tip, which was a short piece of metal wire dipped into the mixture. Totally three Hg/HgO reference electrodes were built for this project and each used a different measuring tip as Zr, Pt, and Ag. The performance of the three Hg/HgO reference electrodes is discussed in Appendix B. The measuring tip was spot-welded onto a copper wire for conduction purposes. The Hg/HgO mixture was then buried by zirconia sand, which damped the pressure from volume expansion of the mixture at high temperature. The open end of the YSZ tube was sealed with zirconia paste manufactured by Cotronics. The paste was additionally covered with epoxy for protection.
Fig 4.1: Structure of one Hg/HgO RE constructed for this project.
4.4 Cyclic polarization

The three-electrode cell used for hydrogen charging in the NaOH-KOH melt includes: a working electrode (WE), which was the Ni-coated Zr-2.5Nb sample; a counter electrode (CE), which was a piece of Ni wire; and the Hg/HgO reference electrode (Hg/HgO RE). A PARSTAT 2263 potentiostat was connected with the cell to control and record the hydrogen charging process. To decide the charging voltage, a cyclic polarization curve was produced first, which indicated the possible reactions at varying potentials. The sweep started from 0.05 V above the open circuit potential (OCP), reversed at 0.3 V below the OCP, and stopped at 0.1 V above the OCP. The potential step height was 2 mV and scan rate was 2 mV•s$^{-1}$. The OCP was measured for 150 seconds before the sweep started. After the cyclic polarization, the nickel layer plated on the sample surface changed to a black colour and started to peel off. For comparison, cyclic polarization curves were also generated for other working electrodes, including Pt, Ni, and Zr-2.5Nb with no Ni plating. The results of the cyclic polarization are summarized in Section 5.1.

4.5 Potentiostatic charging

By analyzing the cyclic polarization curve, the equilibrium potential of hydrogen evolution was estimated and potentials were selected for the potentiostatic charging. Details of the equilibrium potential estimation are covered in Chapter 5. Based on the equilibrium potential and selected potential, a required overpotential can be achieved. For comparison, samples were charged at different potentials for different periods of time. The results of charging are described in Section 5.2. As in the cyclic polarization, the temperature of the NaOH-KOH melt was maintained at 300$^\circ$C. During the charging, the reaction chamber was kept purging with wet nitrogen gas. After the NaOH-KOH mixture transformed into liquid state, the three-electrode cell was lowered into the melt. The charging process started 30 minutes later to allow the electrodes to reach a steady state in the melt.
4.6 Sample preparation for optical microscopy

After potentiostatic charging, the sample was taken out of the melt and cooled down naturally to room temperature. Subsequently, deionized water was used to clean the sample surface. The sample was then molded in epoxy. The radial-circumferential (RC) plane was polished for hydride observation. Table 4.2 lists the polishing sequence.

Table 4.2: Grinding and polishing sequence for epoxy molded samples.

<table>
<thead>
<tr>
<th>Polishing Sequence</th>
<th>Polishing Surface</th>
<th>Abrasive/Size</th>
<th>Load</th>
<th>Base Speed</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CarbiMet 2 abrasive discs (waterproof paper)</td>
<td>320 Grit</td>
<td>2 lbs</td>
<td>100 rpm</td>
<td>Until plane</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>600 Grit</td>
<td>3.5 lbs</td>
<td>150 rpm</td>
<td>4 min</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>1200 Grit</td>
<td>3.5 lbs</td>
<td>150 rpm</td>
<td>10 min</td>
</tr>
<tr>
<td>4</td>
<td>UltraPad cloth</td>
<td>9 µm</td>
<td>3.5 lbs</td>
<td>150 rpm</td>
<td>10 min</td>
</tr>
<tr>
<td>5</td>
<td>TriDent cloth</td>
<td>3 µm</td>
<td>3.5 lbs</td>
<td>150 rpm</td>
<td>10 min</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>1 µm</td>
<td>3.5 lbs</td>
<td>150 rpm</td>
<td>10 min</td>
</tr>
<tr>
<td>7</td>
<td>MicroCloth</td>
<td>0.05 µm</td>
<td>3.5 lbs</td>
<td>150 rpm</td>
<td>3 min</td>
</tr>
</tbody>
</table>

The sample was ultrasonically cleaned with deionized water for 5 minutes between each step of the polishing. After the 0.05 µm MicroCloth polishing, the surface was ultrasonically cleaned with soapy water for better removal of the diamond paste, which was used together with the MicroCloth plate. After drying, the surface was then etched with an etching solution of 3 %wt HF and 15 %wt HNO₃ for 12 seconds. The etched surface showed no contrast under the optical microscope. But after an additional 5 minutes polishing with the 0.05 µm MicroCloth, the image was significantly improved and great contrasts could be seen.
5. Results and discussion

5.1 Cyclic polarization curve analysis

The cyclic polarization curve indicates the presence of cathodic reactions, such as water reduction and trace oxygen reduction on the metal surface at different potentials. Among the reactions detected by the curve, the hydrogen evolution reaction is the only one required for the hydride formation. In this reaction, water molecules in the NaOH-KOH melt dissociate and produce hydrogen atoms on the WE terminal [53]:

\[ \text{H}_2\text{O} + \text{e}^- \rightarrow 0.5 \text{H}_2 + \text{OH}^- \]  

(13)

The hydrogen atoms were adsorbed by the Zr-2.5Nb sample immediately and then absorbed.

\[ \text{H} + \text{Zr} \rightarrow \text{Zr-H}_{\text{ads}} \]  

(14)

To hydrogen charge the sample with a required overpotential, the equilibrium potential of the hydrogen evolution reaction (Reaction 14) should be determined first. According to the Nernst Equation, this equilibrium potential can be calculated as:

\[
E = E^\circ - \frac{2.3RT}{F} \log \left( \frac{P_{\text{H}_2}^{0.5}}{a_{\text{OH}}^{a_{\text{H}_2}}} \right)
\]

(15)

which can be simplified to:

\[
E = -0.828 - \frac{2.3RT}{2F} \log(P_{\text{H}_2}) - \frac{2.3RT}{F} \log(a_{\text{OH}}) + \frac{2.3RT}{F} \log(a_{\text{H}_2})
\]

\[
= -0.828 - 0.057 \times \log(P_{\text{H}_2}) + 0.114 \times \rho\text{OH}^- + 0.114 \times \log(a_{\text{H}_2})
\]

(16)

Thus, to calculate the equilibrium potential of the hydrogen evolution reaction in the NaOH-KOH melt, the \( P_{\text{H}_2} \) at the WE terminal, the \( \rho\text{OH}^- \) of the melt, and the activity of water molecules in the melt are required. Unfortunately, due to the lack of data for these three parameters in the
NaOH-KOH melt, the equilibrium potential can not be calculated by the Nernst Equation. Instead, the potential was estimated empirically. Fig 5.1 shows a cyclic polarization curves for a Pt WE in the melt at 300°C.

![Cyclic Polarization Curve](image)

**Fig 5.1:** The cyclic polarization curve for a Pt WE in NaOH-KOH eutectic melt at 300°C.

The curve covered a potential range from -0.1 to -1.5 V. It started at 0.05 V above the OCP and finished at 0.1 V above the OCP. The reverse potential was set to be 1.2 V below the OCP. The OCP was measured as -0.215 V, using the Hg/HgO RE. The backward sweep of the curve is of interest and can be divided into three parts: the oxygen evolution part, the hydrogen evolution part, and the flat oxygen reduction part in between. The red circle on the boundary between the hydrogen evolution and oxygen reduction parts indicated the region where the equilibrium point of hydrogen evolution reaction may hide.

It is known that at equilibrium, the total current density for the hydrogen evolution reaction was zero. After the equilibrium point in the backward sweep, the current density for the reaction should gradually increase, but still be relatively tiny compared with the one for the oxygen
reduction reaction. Thus it is impossible to tell the exact location of the hydrogen equilibrium point on the curve due to the masking interference from the oxygen reduction reaction. Additionally, in the backward sweep, at about -0.95 V, a moderate peak was detected, which was considered to be the reduction of nickel ions in the NaOH-KOH melt, depositing a nickel layer on the Pt surface. This reaction also created a strong interfering current density, which was even larger than the oxygen reduction current density. The hydrogen evolution current density continued to increase as the potential was swept to more negative region, and eventually got strong enough to identify itself from these interferences. The high current densities and reaction rates of the hydrogen evolution part are considered physically dangerous for the hydrogen charging, and its overpotentials are too large for the project.

It is considered that the nickel beaker released some nickel ions to the NaOH-KOH mixture in the melting step and these nickel ions deposited on the Pt surface when the potential crossed over the -0.95 V region in the backward sweep. This deposited nickel layer then experienced passivation after the reverse point in the forward sweep, forming a layer of nickel(II) oxide (NiO) on the Pt surface. This NiO layer had an OCP value about -0.77 V in the NaOH-KOH melt, which was proven later by the cyclic polarization of nickel coated working electrodes. As a result, a sharp peak at about -0.77 V was detected on the forward sweep. This explains why this sharp peak did not appear on the backward sweep. Immediately after the NiO OCP peak at about -0.77 V on the forward sweep, the current density changed to positive and reached a climax at about -0.7 V. It then quickly dropped below zero again and reached another peak at about -0.66 V. This process is suspected to be related to some unknown reactions between nickel and nickel oxides, which may involve nickel oxides at higher oxidation states.

Fig 5.2 shows two cyclic polarization curves for a nickel plated Zr-2.5Nb sample. Fig 5.2a shows the first polarization cycle of the sample and Fig 5.2b shows the second one, performed after the first one on the same sample in the same batch of melt.
Fig 5.2: The cyclic polarization curves for a nickel plated Zr-2.5Nb sample (a) first polarization cycle; (b) second polarization cycle.
Both curves in Fig 5.2 possessed a large hydrogen evolution part, which was very obvious below -1.0 V. Since the nickel plated sample had a different OCP from Pt in the melt (-0.77 V vs -0.215 V), the flat oxygen reduction regions in Fig 5.2 were much shorter compared with the one in Fig 5.1. Similar to Fig 5.1, it is challenging to determine the exact hydrogen equilibrium location in Fig 5.2. The red circled region between the hydrogen evolution part and the OCP is of interest and a suitable charging potential should lie in this region. A potential value of -0.85 V, which was the closest potential to the OCP on the flat oxygen reduction part of the curve, was selected as the starting point of the testing. During the cyclic polarization, it was observed that a small amount of bubbles began to appear on the WE surface after the potential swept below -0.85 V. Large amount of bubbles were generated when the curve proceeded to the hydrogen evolution part. The bubbles were considered to be hydrogen gas. Thus it is assumed that at -0.85 V on the backward sweep, the hydrogen evolution reaction was initiated and -0.85 V was close to the equilibrium potential of the reaction.

The OCP in the second cycle was about 0.2 V lower than that in the first cycle. This is probably due to the oxidation of the nickel coating in the forward sweep of the first cycle. In addition, for each cycle, the OCP shifted to the more negative side in the forward sweep, which might also be one of the results for the Ni coating oxidation.

The chemical composition and equilibrium status of the melt is considered to be constant during the polarization cycles. This is based on the fact that the surface areas of the WE and CE were small and the time of the polarization cycles was short. More importantly, the consumption of water during the polarization is considered to be made up by the wet nitrogen gas. Thus, the consumption of water molecules and other ions during the polarization cycles is considered negligible. The cyclic polarization curves are found reproducible for the region of interest throughout the experiments. Appendix C shows a series of cyclic polarization curves for comparison and discusses their reproducibility.
5.2 Potential selection for hydride precipitation

After estimating the equilibrium potential of the hydrogen evolution reaction on the cyclic polarization curve, it is time to choose an overpotential for the hydrogen charging. Since the main goal for this project is to test the feasibility of hydrogen charging Zr-2.5Nb material with a low overpotential, it is necessary to choose a voltage value more negative and close to the equilibrium potential as much as possible.

In the early stage of the project, several voltages near -0.85 V were tested potentiostatically. But due to the lack of experience on hydrogen charging and surface treatment, no hydrides were confirmed and the appearance of hydrides on the studied surface remained unknown. To gain a clear vision of the hydrides on the Zr-2.5Nb samples, a charging voltage of -0.985 V was then selected for the hydrogen charging, which was very close to the hydrogen evolution part on the cyclic polarization curve. The corresponding overpotential was -0.135 V. This high overpotential ensured the occurrence of hydriding and guaranteed the existence of hydrides on samples. After some improvement on the surface treatment techniques, a clear vision of hydrides under optical microscope was obtained. The optical analysis gave a clear image of what the hydrides looked like on the polished surface and provided a reference for hydride searching. In the next stage, the overpotential of -0.135 V was reduced and the strategy used to adjust the potential was trial and error. Since -0.985 V is confirmed as an effective voltage for hydrogen charging, the target voltage span is limited between -0.85 V (the estimated equilibrium potential) and -0.985 V. The second voltage for testing could be -0.918 V, which was the mean value between -0.985 V and -0.85 V. If the voltage of -0.918 V precipitated hydrides in the sample, then subsequently the third voltage for testing could be -0.884 V, which was the mean value between -0.918 V and -0.85 V; if it didn’t, then the third voltage would be -0.952 V, which was the mean value between -0.918 V and -0.985 V. By repeating in this sequence, an optimal overpotential sufficient for hydride formation can be achieved eventually. The next section includes several tested voltages and their results for hydrides observation.
5.2.1 Charging voltage No.1: -0.985 V

As mentioned previously, the voltage of -0.985 V creates an estimated overpotential of -0.135 V, which is the highest overpotential used in this project. Samples charged using -0.985 V were found to have a layer of hydrides accumulated beneath the surface. The thickness of the hydride layer depends on the cumulative charge densities. For comparison, two cumulative charge densities were achieved using this potential: 30 C•cm\(^{-2}\) and 90 C•cm\(^{-2}\).

Fig 5.3 shows the current density and cumulative charge density curves for a 30 C•cm\(^{-2}\) trial. The cumulative charge density was in a linear relationship with the charging time, approximately. If the cumulative charge density kept increasing, eventually this relationship turned into a non-linear one, which can be seen in the 90 C•cm\(^{-2}\) trials in Fig 5.4. The current density curve was more complex and sensitive. In this 30 C•cm\(^{-2}\) trial, the current density gradually decreased from -4.8 mA•cm\(^{-2}\) to about -4.2 mA•cm\(^{-2}\) and then increased again. In the 90 C•cm\(^{-2}\) trial, the current density gradually increased with time for the entire charging process.
Fig 5.3: The current density curve (a) and cumulative charge density curve (b) for the nickel plated Zr-2.5Nb sample charged at -0.985 V till 30 C•cm⁻².
Fig 5.4: The current density curve (a) and cumulative charge density curve (b) for the nickel plated Zr-2.5Nb sample charged at -0.985 V till 90 C·cm⁻².
Fig 5.5b shows the cross-section of the sample charged till 30 C•cm⁻² under optical microscope, together with a reference in Fig 5.5a, which is a sample polished with the same method but with no Ni plating nor hydrogen charging. The white layer at the edge of the sample in Fig 5.5b is the plated nickel, which does not exist on the sample in Fig 5.5a. As measured in the feasibility test, the thickness of this nickel layer is about 4 or 5 µm. In Fig 5.5b, there exists a layer of hydrides beneath the Ni coating, which is about 35 µm thick and darker than the internal metal bulk. Similar to previous studies on hydride precipitation from the literature, the hydrides formed using -0.985 V accumulated in a thin layer under the surface, instead of spreading around evenly in the entire sample. This layer of hydrides did not show a great contrast with the metal bulk under optical microscope without etching, and could not be distinguished if the light source was too strong.
Fig 5.5: An optical micrograph for the cross-section of (a) the sample as received; (b) the sample charged till 30 C·cm$^{-2}$. 

Hydride layer
As mentioned earlier, the thickness of this hydride layer is found to be related to the cumulative charged density. Fig 5.6 shows a comparison of the two samples charged at -0.985 V, till 30 C•cm\(^{-2}\) and 90 C•cm\(^{-2}\), respectively. Similar to the sample charged till 30 C•cm\(^{-2}\), the sample charged till 90 C•cm\(^{-2}\) also possessed a thin layer of hydrides beneath the Ni coating. However, the thickness of this hydride layer was about 100 µm, which was about three times of that for the sample charged till 30 C•cm\(^{-2}\). Thus, with further work required, it can probably be anticipated that using the same charging voltage, the thickness of the hydride layer is in a linear relationship with the cumulative charge density.

Another finding in Fig 5.6 is the crack lines cutting through the hydride layer of the 90 C•cm\(^{-2}\) sample. To polish its radial-circumferential (RC) plane, the sample was placed in a sample holder, which consisted of two stainless steel metal plates and squeezed the sample in between. The crack lines were observed after the polishing. With hydrogen entry, the hydrided layer should have an increased internal compressive stress. Since the sample had an arc shape, the squeezing by the sample holder should create compressive stress on one side of the sample and tensile stress on the other side. It is presumed that the tensile stress was much larger than the internal compressive stress caused by the hydriding and led to the cracking.

It is found that the lengths of the crack lines are quite close to the thickness of the hydride layer. Fig 5.7 shows another crack line found on the 90 C•cm\(^{-2}\) sample. The crack line penetrated most of the hydride layer and ended before reaching the internal bulk part. This corresponds with the weaker tensile strength of hydrides and is consistent with the intensive accumulation of hydrides in this subsurface layer.
Fig 5.6: The optical micrograph for the cross-sections of the samples charged at -0.985 V till (a) 30 C cm⁻²; (b) 90 C cm⁻².
Fig 5.7: A crack line found on the optical micrograph for the cross-section of the sample charged at -0.985 V till 90 C•cm².

The images above were taken under optical microscope without etching and lack of great contrast until the etching method in Section 4.6 was proven to be efficient. The etching solution contains 3 %wt HF and 15 %wt HNO₃. After 12 seconds immersion in the solution, the polished surface turns totally black and no contrast can be seen. However, after an additional 5 minutes polishing on the 0.05 µm MicroCloth, significant contrasts presented on the surface and the hydrides showed a quite different colour compared with the metal bulk. Fig 5.8 shows an etched sample charged at -0.985 V till 30 C•cm² (Fig 5.8b), together with an image of the same sample before etching (Fig 5.8a). It is found that after etching, the hydrides layer turns to a darker colour than the internal metal bulk. Among the interface between the hydride layer and the internal metal bulk, short meandering black lines were found and considered to be the traces of hydrides. Appendix D shows several zoom-in pictures of these hydride lines in the 90 C•cm² sample. Tiny
amount of these black hydride lines exists in the internal metal bulk, while most of them remain intensively packed in the darker hydride layer beneath the surface. This indicates that at -0.985 V, the speed of hydrogen entry to the sample is larger than the hydrogen diffusion speed in the bulk part, resulting an accumulation of hydrides near the surface. More images for the 90 C•cm$^{-2}$ sample are included in Appendix E. If the sample was left charging for a long enough period of time, eventually it may become fully saturated with hydrides and the dark hydride layer may occupy the entire RC plane. Thus, it is necessary to reduce the voltage and charge with a lower overpotential, which introduces the second charging voltage of -0.930 V.
Fig 5.8: The optical micrograph for the cross-section of the sample charged at -0.985 V till 30 C•cm$^{-2}$ (a) before etching; (b) after etching.
5.2.2 Charging voltage No.2: -0.930 V

The next voltage tested was -0.930 V, which gives an estimated overpotential of -80 mV. The charging process was more complicated, compared with the -0.985 V trials. Fig 5.9 shows the current density and cumulative charge density curves for the -0.930 V trial. One significant difference presented in this trial is the extremely small current density during the charging, which results a quite low cumulative charge density by the end of the charging process. The current density in this trial ranges from -0.5 to -1.5 μA•cm⁻² and is at least 4000 times smaller compared with those of the -0.985 V trials. The final cumulative charge density only reached 0.02 C•cm⁻², which was drastically lower, compared with the 30 C•cm⁻² and 90 C•cm⁻² reached in the -0.985 V trials. The total charging period was about 18000 seconds. At about 6600 seconds, due to the extremely small current density, which was about -0.932 μA•cm⁻², the charging voltage was adjusted from -0.930 V to -0.950 V. Accordingly, the current density increased to -1.06 μA•cm⁻². At about 7000 seconds, the charging voltage was added with another -7 mV, reaching -0.957 V, and the current density increased to -1.14 μA•cm⁻². It finally reached -1.45 μA•cm⁻² by the end of the experiment.

The cause of this low current density in the -0.930 V trial remains as a puzzle. As mentioned in Section 5.1, the voltage of -0.930 V falls onto the reduction peak of nickel ions around -0.95 V in Fig 5.1. At this potential, the dissolved nickel ions in NaOH-KOH melt should get reduced and deposit on the WE surface, generating a reduction current. The current density measured by the potentiostat should include three reactions: the hydrogen evolution reaction, nickel ion reduction reaction, and oxygen reduction reaction. But the maximum current density in the -0.930 V trial is only -1.14 μA•cm⁻², which is much smaller than expected. One possible explanation is that the reduction of nickel ions did not occur in this trial. In some of the cyclic polarization curves obtained, the nickel ion reduction peak disappeared and this is probably due to the absence of nickel ions in the melt. Unfortunately, the parameters which affect the presence of nickel ions in the melt still remains unknown at this moment.
After polishing, the sample is found to have a small amount of hydrides precipitated on the RC plane. Fig 5.10 shows the RC plane of the sample before and after etching under optical microscope.

As can be seen, there are much less hydrides in Fig 5.10, compared with the samples from the -0.985 V trials. This is within expectation due to the small cumulative charge density and current density. The hydride lines gain a better contrast after etching. One major finding in this trial is that the hydrides no longer accumulate in a thin layer beneath the nickel coating. Instead, the hydride lines spread out and reached the internal metal bulk. This means that the hydride precipitation speed in this trial is lower than those in the -0.985 V trials and should be more related to the hydrogen diffusion rate in the metal bulk. In other words, the internal hydride precipitation rate is more controllable with the charging voltage of -0.930 V.

Although the hydride lines spread widely in the metal bulk, their distribution is still not even through the entire sample. Some locations of the sample are found to have more hydrides than others. Fig 5.11 shows the hydride-rich corner on the RC plane. This top left corner has many long, irregular, meandering hydride lines. Some of them are even longer than 100 µm and reached quite far away from the edges. While on some other corners, almost no hydride lines can be observed. This is probably due to the different internal residual stresses within the sample. As mentioned earlier, hydrides tend to concentrate in areas with larger local stress. The top left corner may have larger local stress, accumulating more hydrides. A similar phenomenon is observed in the -0.985 V trials as well: more hydrides are found along the two hoop edges of the sample than the two radial edges, which can be seen in Appendix D. It is inferred that local stresses along the hoop edges of the sample are larger than those along the radial edges.
**Fig 5.9:** The current density curve (a) and cumulative charge density curve (b) for the nickel plated Zr-2.5Nb sample charged at -0.930 V.
Fig 5.10: The optical micrograph for the cross-section of the sample charged at -0.930 V (a) before etching; (b) after etching.
**Fig 5.11:** The optical micrograph for the hydride-rich corner of the cross-section of the sample charged at -0.930 V.
5.2.3 Charging voltage No.3: -0.875 V

The third voltage tested for hydrogen charging is -0.875 V, which is 25 mV below the estimated equilibrium potential for the hydrogen evolution reaction. Two nickel plated Zr-2.5Nb samples were charged at this potential in two batches of NaOH-KOH melt. The charging processes of the two trials show significant differences. Fig 5.12 shows the current density and cumulative charge density curves for the two trials, with the blue curves representing the first sample and the green curves representing the second one.

The major difference between the two trials is again the current density. For the first sample, the current density has an initial value of -0.413 mA/cm², a minimum value of -0.355 mA/cm², and a maximum value about -1.13 mA/cm². In comparison, for the second sample, the current density has an initial value of -0.39 mA/cm², a minimum value of -0.31 mA/cm², and a maximum value of -0.556 mA/cm², which is about half of that for the first sample. Due to the difference in current densities, although the green trial lasted much longer than the blue one, the difference between their cumulative charge densities is only 0.834 C/cm². The blue trial lasted for about 7200 seconds and the final cumulative charge density was -6.89 C/cm². The green trial lasted for about 16000 seconds, which is more than twice that of the blue trial. Its final cumulative charge density is only -7.719 C/cm². The two trials have similar trends for the cumulative charge densities, only with the blue trial dropping faster.
Fig 5.12: The current density curves (a) and cumulative charge density curves (b) for the two nickel plated Zr-2.5Nb samples charged at -0.875 V.
One possible reason for the low current density of the green trial is the absence of the nickel ion reduction reaction. As mentioned in Section 5.2.2, the reduction of nickel ions in the NaOH-KOH melt can largely affect the current density measured by the potentiostat, and presumably, change the catalysis for the hydrogen evolution reaction. If there were no nickel ions in the melt, the current density measured should be relatively smaller and more stable than those with the ions. The green trial has relatively smaller and more stable current density curve than the blue one. Thus there is a chance that the nickel ion reduction took place in the blue trial but did not in the green one. However, in this case, even with nickel ions in the melt, the nickel ion reduction still may not happen, which makes it unable to explain the current density difference in the two trials. Since the charging voltage of -0.875 V falls on the starting point of the nickel ion reduction peak on Fig 5.1, which ranges from -0.875 V to -1.05 V and peaks at -0.930 V, the possibility of nickel ion reduction occurring at this charging voltage remains debatable. This means that at -0.875 V, nickel ions in the melt may not get reduced and generate the reduction current.

Another possible explanation for the current density difference in the two trials may hide in their water concentrations. Water molecules in the NaOH-KOH melt are considered to be the hydrogen supplier and a crucial part of the complex equilibrium in the melt. They are the most important electroactive species in the melt and the limiting current density is directly related to their concentration in the melt. Thus if the water concentration in the green trial was lower than that in the blue trial, it is possible for the green trial to have a relatively lower current density. The impact of water concentration on the current density may also be one cause of the extremely low current density in the -0.930 V trial. Although batches of NaOH-KOH melt were prepared using the same procedure, there still exist many parameters possible for changing the water concentration of the melt. The water concentration in the -0.930 V trial may be relatively lower compared with other trials, thus led to the smallest current density observed in this project.
Unfortunately at this stage there is no method available to monitor or measure the water concentration in the melt directly.

Samples from the two trials are found to have hydrides precipitated after polishing and etching. Fig 5.13 shows the RC plane of the sample from the blue trial under optical microscope.

**Fig 5.13:** The optical micrograph for the cross-section of the first sample charged at -0.875 V, after etching.

Similar with other etched samples shown previously, the black and irregular meandering lines represent the hydrides. The hydrides precipitated in this sample did not accumulate in a layer beneath the nickel coating. Instead, they spread out in the metal bulk part quite well and can be seen in most area of the cross-section. Although the distribution is still not uniform, this sample is the first one that is confirmed with the existence of hydrides in the central bulk. Appendix F shows more images of the sample, including the central bulk part. By comparing the images in
Appendix F, it is found that hydride lines in the central metal bulk are relatively shorter than those along the edges. In addition, more hydride lines are found near the hoop edges than the radial edges.

Similar results are reported by the sample from the green trial. This is within expectation since the two trials have similar cumulative charge densities and identical charging voltages. Fig 5.14 shows a couple of images of the green trial sample after polishing and etching. Again, hydrides spread into most area of the cross-section, including the central bulk part. More images of this sample can be seen in Appendix G.

The two samples charged by -0.875 V are considered to be the most successful ones obtained so far. Hydrides in these two samples did not concentrate in a thin layer beneath the surface; instead, they spread out to most of the sample, which satisfied the requirement of this project and proved the effectiveness of the charging method. The scattered distribution of hydrides in the two samples tells that the hydrogen entry rate through the sample surface is more or less equal to the hydrogen diffusion rate in the metal bulk. Theoretically, the hydrogen diffusion rate can be calculated according to the Fick’s Law. With a hydrogen diffusion coefficient about $1.7 \times 10^{-6}$ cm$^2$•s$^{-1}$ at about 300°C obtained from the literature [54], the hydrogen diffusion rate was roughly calculated to be around 0.22 mg•m$^{-2}$•s$^{-1}$. Assuming the hydrogen entry rate to be equal to the diffusion rate, a two-hour potentiostatic charging process at -0.875 V can introduce about 0.6 mg of hydrogen into the sample, which gives an total hydrogen concentration about 620 ppm.

To further reduce the overpotential, a final charging voltage was tested, which is discussed in the next section.
Fig 5.14: The optical micrograph for the cross-section of the second sample charged at -0.875 V, after etching.
5.2.4 Charging voltage No.4: -0.850 V

The final voltage tested is -0.85 V, which is close to the estimated equilibrium potential of the hydrogen evolution reaction in the melt. The purpose of testing this voltage is to test the assumption and further explore the possibility of reducing the overpotential. One sample charged at -0.85 V and its results are discussed in this section. Fig 5.15 shows the current density and cumulative charge density curves for the sample. As can be seen, the current density curve of this sample has its unique trend which has never been observed in previous trials. Instead of dropping to the more negative side, the current density remained relatively constant during the first 500 seconds and slowly decreased after. The current density reached -0.493 mA•cm⁻² at about 2000 seconds. The cumulative charge density curve is more or less linear, with a final value of -1.05 C•cm⁻².

The sample from this trial shows presence of hydrides after polishing and etching. Fig 5.16 shows some hydrides on the RC plane of the sample after etching. Based on the amount of hydrides detected on the RC plane, it is considered that the potential of -0.85 V is quite close to the equilibrium potential of the hydrogen evolution reaction. The amount of hydrides observed on this sample is much lower compared with any other sample charged previously. The final cumulative charge density of this -0.85 V trial is larger than that of the -0.93 V trial, which has the lowest value in the testing (1.05 C•cm⁻² vs 0.02 C•cm⁻²), but the amount of hydride lines observed on the RC plane for the -0.85 V trial is much smaller than that for the -0.93 V trial. So it is concluded that the voltage of -0.85V is quite close to the equilibrium potential of the hydrogen evolution reaction in the melt.
Fig 5.15: The current density curves (a) and cumulative charge density curves (b) for the nickel plated Zr-2.5Nb sample charged at -0.85 V.
Fig 5.16: The optical micrograph for the cross-section of the sample charged at -0.85 V.

Again, the hydride lines spread out in the internal metal bulk, instead of accumulating in a thin layer beneath the nickel coating. The distribution of hydrides in the metal bulk was not even as well. The top and bottom right corners of the sample are found to have no hydrides due to unknown reasons. Hydride lines on the central bulk part are confirmed, which can be seen in Fig 5.17.

In addition, the nickel coating on the sample surface is found to experience severe damage. The thickness of the coating is largely reduced after the experiment. Fig 5.18 shows the damaged nickel layer after the experiment. The nickel layer on the bottom surface almost worn through. This indicates that the nickel layer was dissolving at -0.85 V during the experiment.
Fig 5.17: The optical micrograph for the hydride lines on the central bulk part of the sample charged at -0.85 V.

Fig 5.18: The optical micrograph for the damaged nickel layer on the sample charged at -0.85 V.
By reviewing the results from all trials discussed in Section 5.2, it is found that a suitable charging voltage for potentiostatic hydride precipitation in NaOH-KOH melt falls in the range from -0.85 V to -0.875 V. Within this range, the hydride precipitation should have a controllable rate. Scattered distribution of hydrides in the internal metal bulk can be expected and the accumulated hydride layer beneath the surface can be avoided. The potential of -0.85 V in the backward sweep of the cyclic polarization curves is considered to be quite close to the equilibrium potential of the hydrogen evolution reaction in the melt.
6. Conclusions

This thesis investigated the method of electrolytic charging Zr-2.5Nb alloy with hydrogen in moist NaOH-KOH melt at low overpotential. The method is proven to be effective in terms of hydride formation. The equilibrium potential of hydrogen evolution reaction in NaOH-KOH melt is estimated to be slightly higher than -0.85 V, with a Hg/HgO reference electrode using YSZ membrane. It is found that a suitable charging voltage for hydride precipitation in the melt is in the range from -0.85 V to -0.875 V, using the Hg/HgO reference electrodes constructed. Within this range, hydride precipitation should have a controllable rate, which gives a hydrogen entry rate more or less equal to the hydrogen diffusion rate in the metal bulk. This avoids the intensive accumulation of hydrides in a thin subsurface layer. Scattered distribution of hydrides in the internal metal bulk is observed and hydride lines in the central bulk part are confirmed. However, hydride precipitation on samples is found to be uneven, which makes it quite difficult to calculate the total hydride volume fraction using image analysis techniques. One possible solution is to divide the studied cross-section of the sample into small individual cells and use the image analysis techniques to calculate the local hydride volume fractions of the cells, which can then be integrated to obtain the total hydride volume fraction of the entire sample.

In terms of the performance of Hg/HgO reference electrodes, the Hg/HgO RE is considered to be a suitable reference electrode in NaOH-KOH mixture. It provides a stable and reproducible OCP reading around -0.785 V for nickel plated zirconium samples in the melt. The potential difference between Pt and the Hg/HgO RE in the melt is about 0.215 V. The potential difference between Ag, which was the reference electrode used in the previous feasibility test, and the Hg/HgO RE in the melt is about 60 mV. The potential differences between the three constructed Hg/HgO reference electrodes are measured to be lower than 10 mV. The suggested material for the measuring tip buried in the Hg/HgO mixture is Pt. The lifespan of the YSZ RE is considered over 40 hours.
7. Future work

The actual hydride volume fractions of the charged samples were never determined in this project. Since the measuring requires heating the sample over 1000°C to release all the hydride, it is destructive to the tested sample. To gain a clear idea of the amount of hydrides precipitated, samples with different levels of hydride precipitation should be selected and sent to the facility that has the ability to do the volume fraction measurement. This would build a profile between the charging conditions and the resulted hydride amount, which leads to a better control mechanism for the hydrogen charging process.

Disturbance from impurities and oxygen in the melt was never 100% eliminated in this project. Due to the constraints of the experimental apparatus, the NaOH-KOH melt is suspected to be contaminated by nickel ions and oxygen molecules. Renovation on the experiment apparatus is required, including: replacement of the nickel beaker with Pt material; a better seal and deaerating strategy; and an effective method to eliminate the oxygen reducing current.

More Hg/HgO reference electrodes should be built and compared with each other. More electrodes other than Pt and Ag should be tested in the melt to obtain their potential differences against the Hg/HgO RE. A method relating the Hg/HgO RE readings to the SHE potential is required. The surface corrosion of the YSZ membrane should be further studied. A corrosion rate is required to determine the maximum lifespan of YSZ membrane in the melt.

A method of monitoring the water concentration in the melt is required. The water concentrations in different batches should be measured before the experiment starts. More details on the water equilibrium between the melt and the gaseous mixture in the reaction chamber should be studied.
References


APPENDICES

Appendix A: History of pressure tube failure accidents in CANDU [2]

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Date</th>
<th>Failure Cause</th>
<th>Failure Mechanism</th>
<th>PT/GS Type</th>
<th>Replacement</th>
<th>Shutdown</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pickering-3</td>
<td>1974.8.10</td>
<td>Overextended RJ</td>
<td>DHC</td>
<td>Zr-2.5Nb</td>
<td>2 PT</td>
<td>230 days</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 loose GS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pickering-4</td>
<td>1975.5.10</td>
<td>Overextended RJ</td>
<td>DHC</td>
<td>Zr-2.5Nb</td>
<td>52 PT</td>
<td>308 days</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 loose GS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bruce-2</td>
<td>1982.2.9</td>
<td>Overextended RJ</td>
<td>DHC</td>
<td>Zr-2.5Nb</td>
<td>2 PT</td>
<td>112 days</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 loose GS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pickering-3</td>
<td>1983.8.1</td>
<td>GS moved</td>
<td>PT sag</td>
<td>Zircaloy-2</td>
<td>Whole Chanel</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>PT/CT contact</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydride blister</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pickering-3</td>
<td>1985</td>
<td>Overextended RJ</td>
<td>DHC</td>
<td>Zr-2.5Nb</td>
<td>1 PT</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 loose GS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bruce-2</td>
<td>1986.3</td>
<td>Defect during PT fabrication</td>
<td>Fabrication defect</td>
<td>Zr-2.5Nb</td>
<td>1PT/CT</td>
<td>100 days</td>
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<td></td>
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<td>2 loose GS</td>
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<tr>
<td>Wolsong-1</td>
<td>1994.2</td>
<td>Surface crack</td>
<td>Fretting</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4 loose GS</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Pt: Pressure Tube

CT: Calandria Tube

GS: Garter Spring

RJ: Rolled Joint

DHC: Delayed Hydride Cracking
Appendix B: Summary of the Hg/HgO RE performance

The potential of Hg/HgO RE in NaOH-KOH melt were measured empirically against several other electrodes in the melt. Table 5.2 includes the measured potentials of the three Hg/HgO reference electrodes. The three Hg/HgO reference electrodes are named based on their construction dates as YSZ Mk1, YSZ Mk2, and YSZ Mk3, with the internal measuring tip as Zr, Pt, and Ag, respectively. The red background for the first column of Table 5.2 indicates that these electrodes were connected to the positive side (red wire) of the voltmeter during measurement. Oppositely, the green background for the first row of the table indicates that these electrodes were connected to the negative side (black wire) of the voltmeter. Additionally, the numbers in the blue region are average values calculated based on collected data.

Table 5.2: Measured potentials of the three Hg/HgO reference electrodes.

<table>
<thead>
<tr>
<th>Note: all values in volt (V)</th>
<th>VS. Ag</th>
<th>VS. Pt</th>
<th>VS. Ni</th>
<th>VS. Zr</th>
<th>VS. Zr(Ni)</th>
<th>YSZ Mk1</th>
<th>YSZ Mk2</th>
<th>YSZ Mk3</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ Mk1</td>
<td>0.06</td>
<td>0.215</td>
<td>0.804</td>
<td>0.997</td>
<td>0.788</td>
<td>*</td>
<td>-0.009</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(±5mV)</td>
<td>(±5mV)</td>
<td>(±5mV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YSZ Mk2</td>
<td>NA</td>
<td>NA</td>
<td>0.798</td>
<td>NA</td>
<td>0.785</td>
<td>0.11</td>
<td>*</td>
<td>0.0035</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(±5mV)</td>
<td>NA</td>
<td>(±5mV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YSZ Mk3</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>-0.0035</td>
<td>*</td>
</tr>
</tbody>
</table>

By comparing results from YSZ Mk1 and Mk2, it can be seen that they have a very close reading to each other when measured against nickel and nickel plated zirconium electrodes in NaOH-
KOH melt. Their potential difference against nickel electrode and nickel plated zirconium electrode is 6 mV (0.804 V vs 0.798 V) and 3 mV (0.788 V vs 0.785 V). Data against these two nickel related electrodes are the most abundant in the collection, since they are the other two electrodes in the three-electrode cell. The potential difference between YSZ Mk1 and Mk2 was once measured to be 9 mV. The value of 9 mV was measured 4 hours after YSZ Mk1 and Mk2 sunk in the melt. The potential difference between YSZ Mk1 and Ag electrode was once measured to be 60.6 mV. The potential difference between YSZ Mk1 and Pt electrode in the melt was once measured to be 0.215 V, and unfortunately there is no comparison data for Mk2 and Mk3 against Pt electrode.

In terms of survival in the melt, the three Hg/HgO reference electrodes have different service lives. Mk1 is the first one constructed and thus has the longest service time. It has been used in over 16 trials of cyclic polarization or potentiostatic charging. Its estimated service time is at least 50 hours. Mk1 has provided a stable reading in most of its service time. However, it is found that in the last three trials of service, its potential readings against the nickel plated zirconium samples were largely shifted. The potential fell into a range from 0.385 V to 0.519 V and was no longer stable. While in the same trials, Mk2 still provided readings at about 0.78 V. Thus, Mk1 is considered to be malfunctioning and put out of service. The reason for Mk1’s failure remains unknown. It is suspected that the Hg/HgO mixture inside experienced degradation or ran out of one of its components.

Mk2 was constructed after Mk1. It was involved in 8 trials of experiment at least, with an estimated service time over 30 hours. Mk2 still remains functional till the present moment and is the only working Hg/HgO RE left for this project. Both Mk1 and Mk2 suffer from surface corrosion. Their membrane surface contacting with NaOH-KOH melt is found to have small to moderate level of corrosion. The shiny smooth surface of the YSZ membrane is now gone and the internal coarse bulk is exposed. Although the surface corrosion is found to have no impact on the potential readings, it is worried that the membrane may lose its mechanical strength to hold
the high pressure Hg/HgO mixture inside at high temperature. Although it is considered that Mk2 would probably fail first on the electrode element part in the future based on experience from Mk1, it is suggested to keep a close eye on the surface corrosion of the YSZ membrane.

Mk3 is the last Hg/HgO RE constructed for this project and failed before it was used in any trial for polarization or charging. After construction, Mk3 was once compared with Mk2 and their potential difference is amazingly small, only 3.5 mV. However, it is soon found that the potential reading of Mk3 became extremely unstable in later experiments. Its potential reading against other electrodes fluctuated largely, making potential measuring impossible. One possible reason for this failure is the dissolving of the Ag tip in the Hg/HgO mixture. Silver metal can dissolve in mercury, generating a mixture named as silver amalgam [55]. The silver amalgam experienced an aging process after the dissolving, which changed the mixture from liquid to solid phase [56, 57]. Although at 300°C, the amalgam transformed to liquid phase again, the electrical connection to the Hg/HgO mixture became open circuit due to the missing of the Ag tip, causing the failure of the reference electrode.

To summarize the performance of Hg/HgO RE in this project, it is concluded that the Hg/HgO RE servers as a reliable reference electrode in NaOH-KOH melt. It provides a stable reading around 0.785 V against nickel plated zirconium samples in the melt. The potential readings are considered to be stable and reproducible. Although both Zr and Pt works, the suggested material for the measuring tip buried in the Hg/HgO mixture is Pt. Silver tips should not be used for the reference electrode. The expected lifespan is considered over 40 hours. However, for continuous service in the melt, it is suggested to check the surface of the membrane every 2 hours after 10 hours. The YSZ surface is subjected to corrosion due to the high temperature and extreme causticity of the melt. Due to its physical structure, it is impossible to replace the electrode element of the Hg/HgO RE. Once constructed, it should never be disassembled to avoid the potential hazard of mercury. The reference electrode was never tested against thermal shock. However, large and sudden temperature change should always be avoided. It is suggested to cool
down naturally after service. Extreme cautions are required during the construction to avoid potential hazard of mercury. At the end of its lifespan, the Hg/HgO RE should be disposed according to the standard of mercury related waste disposal.
Appendix C: Reproducibility of the cyclic polarization curves

The cyclic polarization curves in this thesis show high level of reproducibility, especially for the backward sweep of the curves. By comparing the cyclic polarization curves in Fig 5.2, Fig C.1, Fig C.2, and Fig C.3, it is observed that all curves have similar trends to each other. They all have an OCP around -0.78 V in the backward sweep, despite of the materials used for the working electrode. Besides, the oxygen reduction parts of the curves, which are the region of interest, cover more or less the same range of potentials. In addition, these trends of the cyclic polarization curves can also be found in Fig 5.1, which uses Pt as WE and covers a relatively wider range of potentials. However, in some curves, the nickel ion reduction peaks can not be identified. The reason for its absence remains unknown at this moment.

Fig C.1: The cyclic polarization curve for another nickel plated Zr-2.5Nb sample in NaOH-KOH melt at 300°C.
Fig C.2: The cyclic polarization curve for a nickel WE in NaOH-KOH melt at 300°C.

Fig C.3: The cyclic polarization curve for another nickel WE in NaOH-KOH melt at 300°C.
Appendix D: Zoom-in optical micrograph for the hydride lines on the cross-section of the sample charged at -0.985 V, till 90 C•cm$^2$

Fig D.1: Boundary between the subsurface hydride layer and metal bulk.
Appendix E: Additional optical micrograph for the sample charged at -0.985V, till 90 C•cm$^{-2}$.
Fig E.1: Thick hydride layer for the central region of the RC surface.
Fig E.2: Reducing thickness of the hydride layer for the region near the radial edges.
Fig E.3: Thin hydride layer near the radial edges.
Appendix F: Additional optical micrograph for the first sample charged with -0.875 V
Fig F.1: Scattered distribution of hydrides in the region near the radial edges.
Fig F.2: Scattered distribution of hydrides in the central region of the RC surface.
Fig F.3: Distribution of hydrides in the central metal bulk.
Appendix G: Additional optical micrograph for the second sample charged at -0.875 V
Fig G.1: Scattered distribution of hydrides in the region near the radial edges.
Fig G.2: Scattered distribution of hydrides in the central region of the RC surface.
Fig G.3: Distribution of hydrides in the central metal bulk.