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Photo-electrochemical Investigation of Radiation-Enhanced Galvanic Coupling and Hydrogen Permeation in TPBAR- related Materials

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EXECUTIVE SUMMARY

Research conducted in FY17 used photo-electrochemical methods to investigate the potential for radiation-enhanced galvanic coupling in tritium-producing burnable absorber rod (TPBAR) materials. Specifically, a laboratory electrochemical cell was coupled with UV light in order to perform electrochemical open-circuit voltage and galvanic current measurements, techniques that have been used successfully in previous studies to replicate galvanic processes in reactor settings. UV irradiation can mimic reactor-like behavior because, similar to both directly and indirectly ionizing radiation, UV photons with energy greater than the band gap of the material will generate free charge carriers (electrons and holes) and can substantially alter the passivating effect of metal oxides. The main conclusions from FY17 are:

1. Significant electrochemical potential differences exist between TPBAR materials
2. Galvanic current flows between these different materials due to these potential differences
3. Potential differences and galvanic currents are enhanced by UV light
4. UV light can simulate radiation-induced charge generation effects in TPBAR materials

These conclusions are notable because galvanic currents are known to drive hydrogen transport and permeation in metals and could be responsible for the increased permeation seen in Watts Bar. Although, electrochemical permeation measurements conducted in FY17 did not have the sensitivity to detect the hydrogen uptake or permeation current due to this galvanic coupling. Finally, it is important to note that radiation-enhanced galvanic coupling between TPBAR materials would be a persistent phenomenon due to activation products, and therefore, is relevant to both normal and off-normal lifecycle events (e.g., disposal conditions, breach during reactor operations). UV light experiments permit relatively simple measurements of enhanced corrosion processes during such conditions.

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LIST OF ABBREVIATIONS

304 SS	304 grade stainless steel
316 SS	316 grade stainless steel
Al-316 SS	Aluminide coated 316 SS (coated cladding)
E_{corr}	Corrosion potential
EDM	Electrical discharge machining
eV	Electron volts
FY	Fiscal year
λ	wavelength
Ni-Zry-4	Nickel plated Zircaloy-4 (getter)
OCP	Open circuit potential
PNNL	Pacific Northwest National Laboratory
SCE	Saturated calomel electrode
SRNL	Savannah River National Laboratory
TPBAR	Tritium-producing burnable absorber rod
UV	Ultraviolet
WBN1	Watts Barr Nuclear Reactor 1
ZRA	Zero resistance ammeter
Zry-4	Zircaloy-4

1.0 Introduction

The tritium permeation rate from irradiated TPBARs into WBN1 reactor coolant exceeds predicted values. While substantial progress has been made toward understanding this process, the mechanisms responsible for the enhanced permeation of tritium seen in reactor settings have yet to be fully identified. A possible mechanism for this increase that warrants investigation is radiation-enhanced galvanic coupling. Galvanic coupling creates a current flow whenever metals come in electrical contact, as the more active metal (anode) transfers electrons to the less active, or more noble, metal (cathode). If the potential difference between the two metals is significant, the anode will experience enhanced oxidative corrosion, while the cathode will see reduced rates of corrosion. This phenomenon is used to protect steel vessels in seawater and other corrosive environments by using sacrificial Zn or Al anodes, which will preferentially corrode and dissolve instead of the steel. However, in hydrogen-containing environments, the cathode will see enhanced rates of hydrogen permeation due to the accumulation of reducing electrons, and therefore, it is important that galvanic currents are avoided in the presence of hydrogen [1]. Galvanic coupling and the resulting corrosion can be minimized by keeping different metals electrically isolated or by only using metals that have similar electrical potentials, though galvanic cells can still form within the same metal due to local effects (e.g., pitting or crevice corrosion).

The TPBARs are constructed of various metallic materials in close contact, which could give rise to galvanic coupling if significant potential differences exist between them (**Figure 1-1**). In most standard conditions, the TPBAR materials (e.g., 316 SS, Ni, Zircaloy-4) are passive, and contact between them should not generate galvanic currents of any consequence. However, passive materials may become active in radiation fields and galvanic processes may result. A notable example is that of “shadow corrosion” observed in zirconium-base alloy structures contained in nuclear reactors [2, 3]. In this case, local enhancements in corrosion occur in zirconium alloys when placed in close proximity to another metal

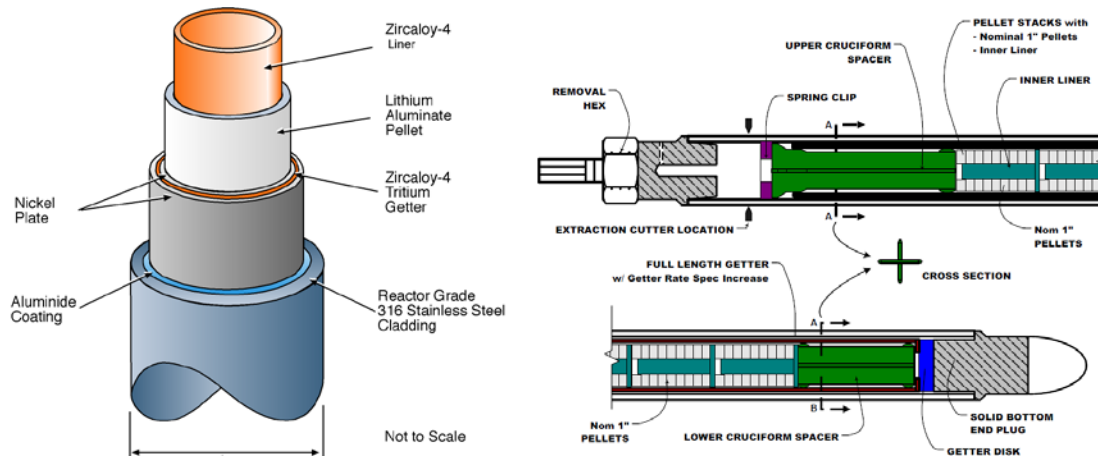


Figure 1-1. Schematics showing the internal components of TPBARs [4].

within a radiation field. The shape of the corroded area on the Zircaloy structure replicates the shape of the other metallic structure; hence the name, shadow corrosion (**Figure 1-2**). While research is ongoing, it has been established that the shadow corrosion effect is galvanic in nature and generally only observed in reactor settings [5]. However, researchers have recently been able to reproduce this galvanic effect in a laboratory setting by using UV light irradiation in an electrochemical cell [6]. In particular, they found that the corrosion potential of Zircaloy-2 was modified by UV light and became much more anodic under irradiation. Further, when Zircaloy-2 was coupled to another metal, such as Inconel or 304 SS, galvanic currents appeared under UV illumination and disappeared when the light was cut off. These results are

notable not only because they elucidate a radiation-enhanced galvanic mechanism, but also because they demonstrate that UV light can be used to reproduce radiation-induced effects within a traditional laboratory setting.

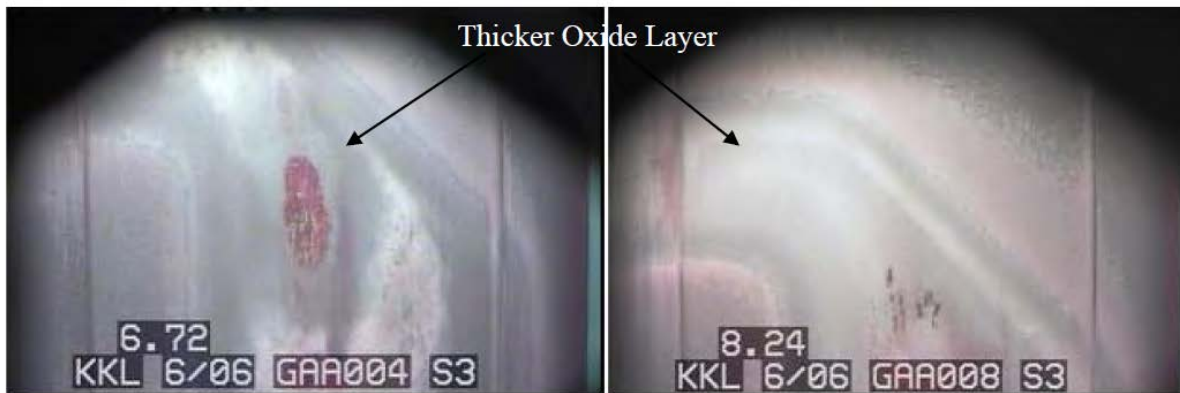


Figure 1-2. Photographs of shadow corrosion on a Zircaloy surface. The oxidation pattern matches the shape of the nearby stainless steel control blade [7].

The researchers in the study described above proposed that the greater than band gap UV light irradiation was able to induce photocurrents in the passivating oxide layers, similar to what was expected to occur in reactor environments with ionizing radiation. The parallel concepts between radiation-induced currents and light-induced currents are not necessarily surprising or controversial, as can be seen in the similarities between the mechanisms behind solid state photodetectors and solid state radiation detectors or the mechanisms of photovoltaics and betavoltaics. Metals are typically protected from corrosion by oxide layers, and such photocurrents or radiation-induced currents reduce the protective or passivating effect of the oxide layers. This is because corrosion, or oxidation, is an electrochemical effect. For example, in order for Zr metal to be oxidized by ambient O_2 gas, four electrons must migrate from the Zr metal boundary through the oxide layer to the surface, while two O^{2-} ions must migrate from the surface to the Zr metal ($Zr + O_2 \rightarrow ZrO_2$). Increasing the number of charge carriers will speed up this process, especially if the charge transfer is a rate limiting step. Therefore, both radiation and UV light can enhance corrosion and galvanic processes in TPBAR materials by creating more charge carriers in the passivating oxide layer of metals.

In summary, the motivation behind this project is to investigate galvanic coupling between TPBAR materials, and to determine whether irradiation can enhance hydrogen permeation rates in these materials. While radiation-enhanced galvanic effects have been observed in Zircaloy materials before, as described above, the coupling between TPBAR materials has not been investigated, nor has its effect on hydrogen permeation. Since galvanic coupling is an electrochemical effect, the investigations are conducted in a photo-electrochemical cell using pure water as a test solution and a high powered UV light source. While such a cell is a laboratory device, background water vapor, other impurity gases (e.g., reactions between CO_2 and H_2), and solid state ionic conduction all could give rise to similar electrochemical effects at large or local scales within the actual TPBARs. Therefore, a UV photo-electrochemical investigation of TPBAR materials can provide insight into the potential for radiation-enhanced galvanic coupling between the different materials, and whether this can lead to increased hydrogen permeation. The results from this study show that galvanic coupling will occur between the different TPBAR materials in the presence of water and that this coupling will be enhanced in reactor environments.

2.0 Experimental Procedures

2.1 TPBAR Material Samples

TPBAR samples were provided by PNNL, including bare cladding (316 SS), aluminide coated cladding (Al-316 SS), the nickel-plated Zircaloy-4 getter (Ni-Zry-4), and the Zircaloy-4 liner (Zry-4). Two types of samples were provided. One type was a full cylinder tube section cut by electrical discharge machining (EDM) to 1.5" in length. These samples were used for some initial scoping tests. The other sample type that was used for the majority of the testing and data described below were also 1.5" sections. However, these were cut by EDM an additional time to create half cylinders, thereby allowing the inner surface to be illuminated with UV light. These samples were used as received with no additional cleaning or treatment step taken before testing. The TPBAR samples were masked with electroplating tape to keep the area exposed to the electrolyte and UV light the same. The exposed area was 0.5 cm². In addition to the TPBAR samples, Ni foil (99.9%, thickness 0.125 mm) and Al foil (99.99%, thickness 0.13 mm) were obtained from Sigma-Aldrich to compare with the TPBAR coating materials. These samples were also used as received and were cut to size before measurement.

2.2 Open Circuit Potential Measurements

Open circuit potential (OCP) measurements were conducted using a Pine WaveDriver 10 potentiostat via the control and measurement software AfterMath. A standard three electrode setup was used, with a saturated calomel electrode (SCE) used as a reference and a Pt coil as the counter electrode. The working electrode was one of the samples described in Section 2.1. These electrodes were immersed in deionized water, which was open to atmosphere but had argon gas bubbled through it. After the open circuit potential of the working electrode stabilized with respect to the reference electrode, data recording commenced. After 10 minutes, the UV light source's shutter was opened, which illuminated the working electrode (sample). The shutter was closed after irradiating the sample for 5 minutes with UV light. The UV process was then repeated three more times (10 minutes incubation, followed by 5 minutes of UV light exposure). During the experiment, the reference electrode was masked to block stray UV light. The counter electrode was not masked, but was placed in a region of low stray light intensity. The UV light source used was a 200 W Hg arc lamp (Omnicure S2000) that delivered light with wavelengths of $\lambda = 250 - 450$ nm (5 - 2.75 eV) to an 8 mm spot with an intensity of 30 W/cm².

2.3 Galvanic Current Measurements

Galvanic measurements were conducted using a Pine WaveDriver 10 potentiostat via the control and measurement software AfterMath, as described above. In this case, the zero resistance ammeter (ZRA) technique was used, which utilizes only two electrodes. Both the working and counter electrodes were one of the samples described in Section 2.1 so that the galvanic coupling between them could be measured. Both electrodes were immersed in deionized water, which was open to atmosphere but had argon gas bubbled through it. Data recording commenced immediately. After 5 minutes, the UV light source's shutter was opened. The UV light shutter was closed after irradiating the sample for 5 minutes, and data recording proceeded for another 5 minutes. Both the working and counter electrodes were placed in the broader, defocused region of the UV spot lamp so that both pieces were equally illuminated, but at reduced intensities. The UV light source used was the 200 W Hg arc lamp described above.

2.4 Hydrogen Permeation Experiment

The hydrogen permeation experiment was conducted using a modified Devanathan-Stachurski technique [8]. The cathodic compartment consisted of a ZRA setup with a Zircaloy-4 liner sample as the counter electrode and Ni foil as the working electrode. Deionized water was used as the catholyte. The galvanic current between these two electrodes were monitored by a WaveDriver 10 potentiostat. The anodic compartment, which was separated from the cathodic compartment by the Ni foil, contained 0.1M NaOH with Ar gas bubbled through it as an anolyte. The reference electrode was Hg/HgO, and a Pt coil was used as a counter electrode. The working electrode was the same Ni foil, except the anodic side of the Ni foil

had a Pd coating applied to the surface. This Pd layer (~150 nm, determined by calibration curve) was separately sputter-coated onto the Ni foil, and is there to quickly oxidize any permeating hydrogen. The Ni foil was polarized potentiostatically to -300 mV (vs. Hg/HgO), while the current in the anodic compartment was monitored as a function of time. The controlled potential setup of the anodic compartment was controlled and monitored by a separate WaveDriver 20 bipotentiostat. The AfterMath software enabled control and monitoring of both potentiostats, which were connected to the same computer. Further details of this experiment are given in Section 3.3.

3.0 Results and Discussion

3.1 Open Circuit Potential Measurements

Galvanic coupling requires three conditions in order to occur: different metals in (1) electrical contact, (2) in the presence of an electrolyte, (3) with significant differences in electrochemical potentials between them. It is important to note that Conditions 1 – 3 are necessary for the galvanic process to occur, while the overall efficiency of the process can depend on other conditions such as temperature, relative areas, etc. TPBARs are known to satisfy Conditions 1 and 2 due to their composition and the release of tritiated water from the lithium aluminate pellets during irradiation, respectively. However, the electrochemical potentials of the TPBAR materials in the presence of water has not been previously recorded. Therefore, these measurement will address whether or not TPBAR materials satisfy Condition 3. Further, insight into in reactor behavior can be obtained by coupling open circuit potential measurements with UV light modulation, as described above.

Figure 3-1 shows the experimentally measured open circuit potential (E_{corr}) versus time for the different test materials (see Section 2.2 for details) in the dark and in UV light. As can be seen in the plots, UV light irradiation noticeably changes E_{corr} for all of the materials, and in some cases the change is substantial. Interestingly, all of the materials, except for the Zry-4 liner, grow more cathodic under illumination, indicating that the native oxide exhibits “p-type” behavior. The Zry-4 liner exhibits “n-type” behavior and grows more anodic. This means that UV light excites electron-hole pairs in the oxide layer, and the majority carrier (holes in the case p-type, electrons for n-type) migrates to the inner metal interface while the minority

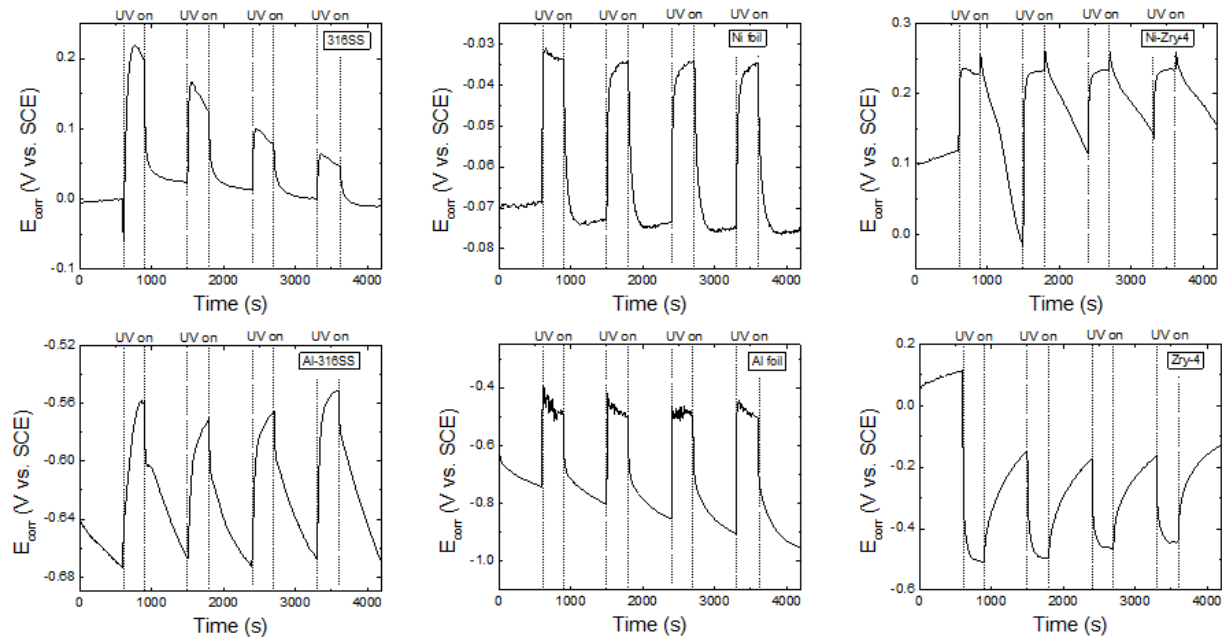


Figure 3-1. Plots showing the open circuit potential versus time for the various TPBAR related materials

carrier (electrons in the case of p-type, holes for n-type) migrates to the exterior electrolyte interface [9]. These surface bound holes make n-type materials more anodic under illumination, and p-type materials grow more cathodic due to the presence of surface electrons. Zry-4 exhibits other interesting behavior besides this opposite carrier response. For example, the Zry-4 is initially fairly passive and has a potential more cathodic than the reference electrode. UV light dramatically shifts the potential to anodic region, increasing the likelihood of oxidation. After the light is turned off, the potential does not revert very quickly to its pre-illumination level, which suggests that charge recombination and migration is very slow and is impeded by defects and deep charge-trapping sites. Similarly slow potential recovery and trapping behavior is observed in the coated samples, Ni-Zry-4 and Al-316 SS. Ni-Zry-4 also shows an interesting mixed response behavior, where anodic and cathodic responses are in competition but are kinetically different. This is seen in the slow downward drift in the potential after the UV light is turned on and the quick spike up after the light is turned off. The origin of such behavior is not clear at this time, but could be associated with coating variations. Finally, it is interesting to note that the coating material (Ni on Zry-4 and Al on 316 SS) on the TPBAR components are electrochemically similar to the pure materials (Ni and Al foils) in that they are close in potential and have the same behaviors under illumination.

In order to satisfy Condition 3 for galvanic coupling to occur, the potential difference between the two connected metals needs to be significant. **Figure 3-2** compares the electrochemical potentials between the different TPBAR and related materials, and the differences can be quite large. Furthermore, these differences can be enhanced by charge generation within the native oxide layers by UV light. Since UV light can inform on the charge generation behavior in radiation environments, it is expected that such potential differences will be enhanced in reactor as well. A general rule of thumb is that in temperature controlled, low humidity environments some bimetallic designs can handle potential differences up to 0.5 V without significant galvanic corrosion [10]. Thus, it is important to note that TPBAR materials can have potential differences greater than 0.5 V at room temperature in the dark, and can further increase to larger differences under illumination (e.g., Ni-Zry-4 vs. Al-316 SS).

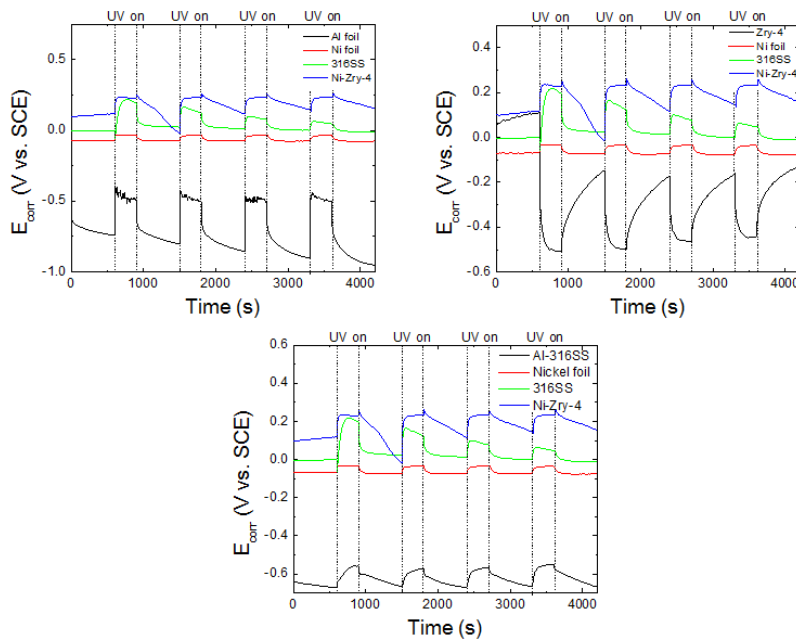


Figure 3-2. Comparison between the electrochemical potentials of the different TPBAR materials comparing the anodic samples with the three most cathodic ones.

3.2 Galvanic Current Measurements

Hydrogen uptake and permeation due to galvanic coupling are related to the current that flows between the cathodic and anodic metals. Therefore, the galvanic current was measured between TPBAR materials that were coupled in deionized water. The galvanic currents between the different materials in the dark and under UV irradiation are shown in **Figure 3-3**. In most cases, an increase in the magnitude of the current is seen when the UV shutter is open at 300 seconds. This photocurrent decreases after the UV light shutter is closed at 600 seconds. In the plots, the material listed first is the working electrode and materials listed

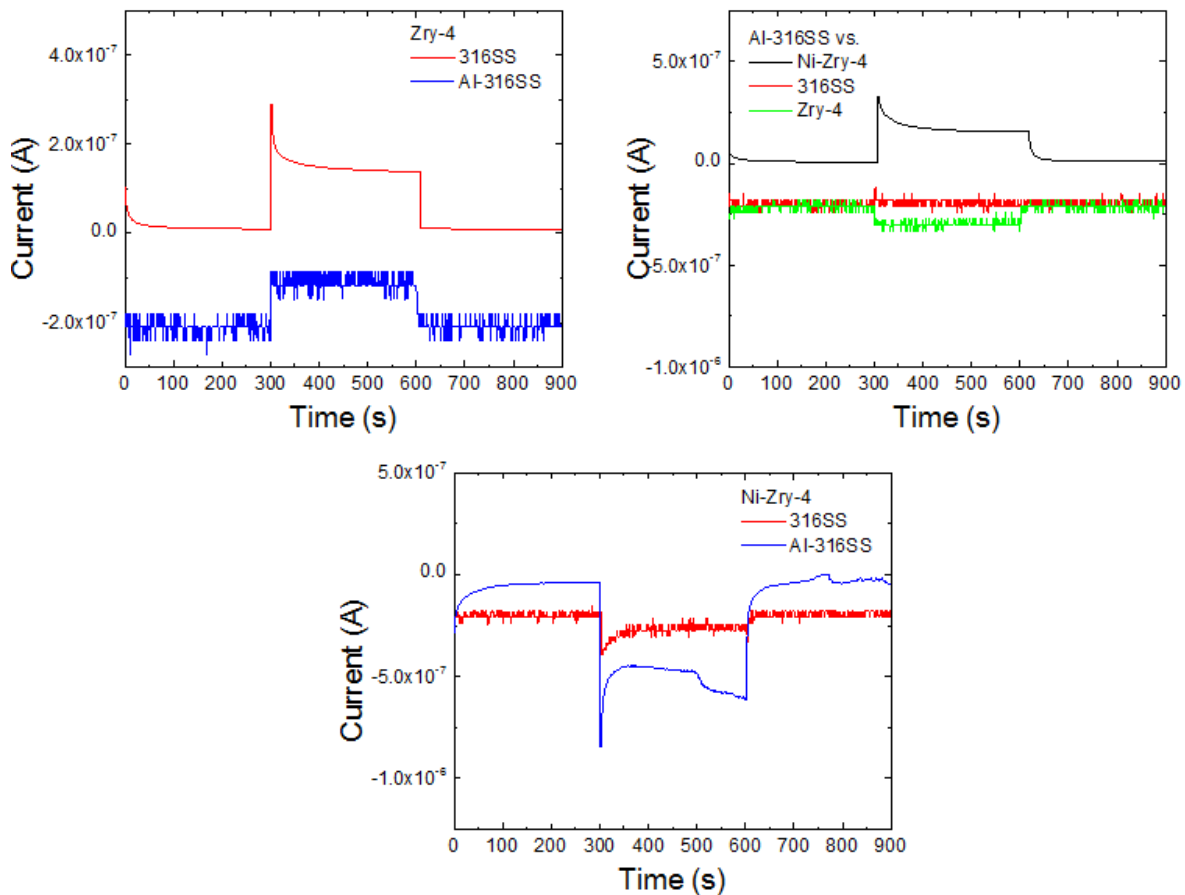


Figure 3-3. Galvanic currents between the different materials in the dark and under UV irradiation

next to the line colors are the counter electrodes. If the current shifts in the positive direction under illumination, this means the working electrode has an anodic current and engages in the oxidation reaction. Correspondingly, if the current shifts in the negative direction, this means that the working electrode has a cathodic current and promotes the reduction reaction in the electrolyte. In pure water, the cathodic current evolves hydrogen, and some proportion of the hydrogen is absorbed into the metal (uptake and permeation). The exact proportion of hydrogen absorbed versus evolved depends on a number of different environmental and material factors. In any case, the cathodic side of the galvanic couple will be the material expected to experience the increase in hydrogen uptake through this mechanism.

Generally, one can then determine which side will have the increased hydrogen uptake by comparing the electrode potentials. The ubiquitous cathodic current seen for Ni-Zry-4 galvanic couples is an example of

a TPBAR material that will see increased galvanic hydrogen uptake since it has the most positive potential of the test materials (**Figure 3-2**). A notable counter-example is the galvanic couple between Zry-4 and Al-316 SS. These two materials have very similar potentials under UV illumination, but a UV light enhanced current flows between these materials, where the Zry-4 is the photoanode and the Al-316 SS is the photocathode. This directional current flow is likely the result of the p-n junction formed between these two materials (photovoltaic effect). For in reactor TPBAR operations, this particular galvanic couple would be problematic as this p-n junction would drive hydrogen through coated cladding since it forms the cathodic side of the couple.

3.3 Hydrogen Permeation Experiment

Experiments were conducted to measure the effect of galvanic cathodic charging on hydrogen permeation. In particular, the permeation experiment was conducted using a modified Devanathan-Stachurski technique [8]. In a typical Devanathan-Stachurski experiment, two individual electrolytic cells are separated by a membrane made from the test material. In the cathodic cell, hydrogen is produced electrochemically by applying a cathodic polarization using a potentiostat. Some of this evolved hydrogen is absorbed into the membrane and permeates through to the other cell, the anodic compartment. In the anodic cell, the hydrogen diffusing through the sample is oxidized at a constant potential, creating an anodic current that is directly proportional to the amount of hydrogen permeating through the membrane. The potential and current measurement on the anodic side is monitored by a separate potentiostat than the one controlling the cathodic side. Generally, the anodic side of the membrane is also coated with Pd to increase the efficiency of the oxidation reaction. The experiments attempted here were similar, except that galvanic currents were used to drive hydrogen permeation instead of cathodic polarization via a potentiostat (**Figure 3-4**). The initial experiment used a Ni foil as a permeation membrane with the Zry-4 liner as the galvanic couple on the cathodic side. The anodic side of the membrane was sputter coated with a 150 nm Pd layer. In our experimental case, the background currents ($\sim 10 \mu\text{A}$) on the anodic side were much larger than the galvanic currents ($\sim 100\text{'s nA}$) on the cathodic side. Thus, the smaller proportional hydrogen permeation current was undetectable in the anodic background. The larger background current on the anodic side is attributed to a relatively unstable Hg/HgO reference electrode and pinholes in the sputtered Pd layer. Though, repeated attempts with thicker Pd sputter coated layers did not yield improved background currents. It is possible to increase the galvanic currents over the background anodic currents by using more aggressive and conductive electrolytes instead of deionized water (e.g., aqueous H_2SO_4 solutions). Alternatively, the standard method of potentiostatic charging could also be used. However, such results would not be directly applicable to TPBAR operational environments.

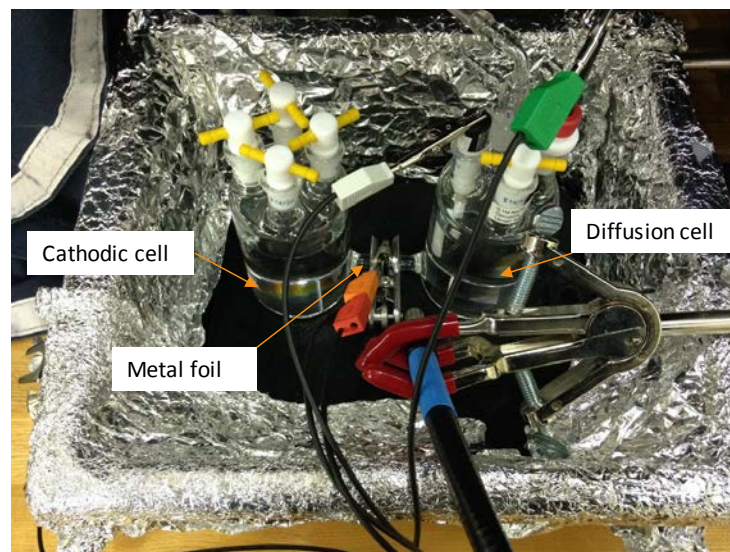


Figure 3-4. Photograph of the modified Devanathan-Stachurski permeation setup.

4.0 Conclusions

Research conducted in FY17 used photo-electrochemical methods to investigate the potential for radiation-enhanced galvanic coupling in TPBAR materials. The major findings are:

1. Significant electrochemical potential differences exist between TPBAR materials
2. Galvanic current flows between these different materials due to these potential differences
3. Potential differences and galvanic currents are enhanced by UV light
4. UV light can simulate radiation-induced charge generation effects in TPBAR materials

Findings 1 – 3 are notable because galvanic currents are known to drive hydrogen transport and permeation in metals and could be responsible for the increased permeation seen in Watts Bar. Even though the electrochemical permeation measurements conducted did not have the sensitivity to detect the hydrogen permeation current, increased uptake and permeation are expected to occur due to these galvanic currents. With regard to Finding 4, UV light experiments are not going to replace data obtained from in reactor experiments. However, such experiments can highlight areas of concern. The galvanic couple of Zry-4 with Al-316 SS is one area of concern highlighted by this study. The cathodic (i.e., hydrogen charging) side of that couple is the Al-316 SS barrier layer. Another area of concern is any metal coupled with the Ni-Zry-4 getter. While the highly cathodic nature of Ni-Zry-4, both in the dark and under irradiation, means that it will form the hydrogen charging side of the galvanic couple as desired, the increased degradation of the anodic side may create a corroded metal oxide surface that is less resistant to permeation.

5.0 Future Work

The summative conclusion of this initial study is that galvanic coupling should occur in the TPBARs during and after irradiation. The magnitude of associated effects are yet to be determined. Future work should extend the test environment to more prototypical conditions by using gas and vapor phases and higher temperatures, as well as by considering the effects of different gases (H_2O , H_2 , CO_2) that may be present in the TPBAR during reactor operations. More sensitive hydrogen uptake measurements should also be used to detect any increase in hydrogen uptake. Finally, radiation-enhanced galvanic coupling between TPBAR materials would be a persistent phenomenon due to activation products, and therefore, is relevant to both normal and off-normal lifecycle events (e.g., disposal conditions, breach during reactor operations). UV light experiments permit relatively simple measurements of enhanced corrosion processes during such conditions and could provide guidance for storage and accident scenarios.

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