Probing the Radial Chemistry of Getter Components in Light Water Reactors via Controlled Electrochemical Dissolution

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Abstract: Getters are among the key functional components in the tritium-producing burnable absorber rods (TPBARs) of light water reactors (LWRs) and are used to capture the released tritium gas. They are nickel-plated zircaloy-4 tubes that, upon exposure to irradiation or tritium in the light water reactors, undergo alteration in structure, chemical composition, and chemistry. Understanding the radial tritium distribution is key to gaining insight into the evolution of new chemistry upon irradiation to predict getter performance. The holy grail is to develop a method akin to selectively peeling off the layers of an onion in an effort to get a radial map of elements and particularly tritium across the getter. Toward this goal, the overall aim of this work is to establish a correlative technique that can be used to determine radial tritium distribution across getters. To this end, this work specifically focuses on the validation of a correlative method for controlled radial dissolution of nickel-plated getters. Here, pristine getters as well as getters loaded with different mass ratios of hydrogen and deuterium are used as the nonradioactive surrogates of tritium, the idea being that the methodology can be readily extended to tritiated getter components. Here, the surface nickel layers as well as the bulk zirconium layers are sequentially dissolved in a controlled, uniform way using voltage-assisted electrochemical dissolution techniques. The dissolution is complemented by periodic elemental analysis of the electrolyte solution during and post dissolution. This is complemented by microscopic analyses on the exposed surfaces to provide a correlative technique for a complete picture of the radial distribution of various elements across the getter.

Introduction

Tritium gas is a key requirement for the nuclear weapons stockpile in the United States, as well as across the globe. However, its short half-life ($t_{1/2} = 12.3$ years) requires its fast replenishment. From 1988 to 1992, the use of three different types of dedicated reactors was considered by the United States Department of Energy for tritium production, namely (i) heavy water reactors (HWRs), (ii) high-temperature gas-cooled reactors (HTGRs), and (iii) light water reactors (LWRs). Subsequently, tritium production was transitioned to commercial LWRs. In the commercial LWRs, tritium is presently produced within tritium-producing burnable absorber rods (TPBARs). The TPBARs hold $\sim 132$ in. of LiAlO$_2$ pellets arranged as a cylindrical tube, and the reaction of $^6$Li with thermal neutron flux generates tritium via reaction 1:\textsuperscript{1,5–8}

$$^6\text{Li} + _0\text{n} \rightarrow ^{\pm}\text{He} (2.05 \text{ MeV}) + ^1\text{H} (2.75 \text{ MeV})$$

(1)

The generated tritium is converted into both tritium gas as well as tritiated water and is contained within the TPBARs by two key functional components, namely liners and getters. Both these components are cylindrical tubes made of Zircaloy-4 (Zr-4), an alloy of zirconium. The liners reduce $^3\text{H}_2\text{O}$ to $^3\text{H}_2$ gas; the gas is no longer blocked by the nickel plating and can now penetrate into the getters to be captured by zirconium in Zr-4 to form zirconium tritide.

This tritide formation causes changes in the structure and morphology of the getter, the extent of the change being dependent on the extent of H/T migration and permeation into the material. As these changes directly affect subsequent getter chemistry and consequently their performance, a key to a better understanding of this chemistry lies in understanding tritium diffusion through the getter; this will be instrumental in designing improved tritium transport models and leading to improved getter design. Consequently, efforts are underway to understand and predict tritium permeation into the TPBAR and their radial distribution within the getter core.

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Supporting Information

1) The getters are coated with an electroplated nickel layer on top of Zr-4, which prevents the penetration of gaseous $^3\text{H}_2\text{O}$. The liners reduce $^3\text{H}_2\text{O}$ to $^3\text{H}_2$ gas; the gas is no longer blocked by the nickel plating and can now penetrate into the getters to be captured by zirconium in Zr-4 to form zirconium tritide.
While several theoretical and simulation studies have predicted tritium migration through getters, and Zr-4 materials in general, experimental studies to probe this behavior at a macroscale are limited in particular by the lack of a proper methodology to probe tritium permeation and migration radially into the getter. A possible way to determine the spatial and radial T/H-distribution within Zr-4 materials can be through the controlled and uniform dissolution of the hydride-loaded getter surface akin to carefully peeling off the layers of an onion, followed by the analysis of the newly exposed surfaces. However, methodologies to probe the circumferential or radial zirconium hydride distribution have mostly involved etching cross-sections by chemical dissolution techniques using harsh corrosives (concentrated nitric acid, hydrofluoric acid) and elevated temperatures, which lacked the ability to control the radial uniformity and rate of dissolution.

Electrochemical dissolution techniques can address the larger deficiencies of chemical dissolution through the ability to use less harsh reactants, adding control and enhancing uniformity of the resulting process. The dissolution rate can further be tailored through modulating the applied electrochemical voltage, current and/or through changes in the electrode material, its area of contact with the active surface, and the electrode configuration. As a proof-of-concept, we recently demonstrated controlled potential electrolytic methods for controlled radial dissolution of Zr-4-based liners. The getter components present a higher complexity due to the presence of the nickel plating. Therefore, responding to the need for a technique for controlled and uniform dissolution of getter surfaces to effectively probe the radial chemistry of the core, the overall aim of this work is to establish a correlative technique that can be used to determine radial elemental distribution across getter-based components of LWRs. The objective of this work is to demonstrate an electrochemical technique and identify the conditions where the surface nickel layers as well as the bulk zirconium layers can be dissolved sequentially in a controlled, uniform way using electrochemical dissolution techniques. A controlled potential method is identified to provide the desirable control of dissolution rates, as demonstrated by multiple methods. The dissolution is complemented by the periodic analysis of the electrolyte solution during and post dissolution as well as complementary microscopic analyses on the exposed surfaces to establish a correlative technique that can provide a complete picture of radial distribution of various elements across the getter.

RESULTS AND DISCUSSION

As mentioned, the objective of this work is to demonstrate an electrochemical technique and identify the conditions where the surface nickel layers as well as the bulk zirconium layers can be dissolved sequentially in a controlled, uniform way using electrochemical dissolution techniques. Therefore, studies were conducted on both unplated as well as Ni-plated getters loaded with hydrogen and deuterium, which served as the nonradioactive and unirradiated surrogates of the tritiated components, allowing ease of operation. The aim was to establish the methodology with nonirradiated components that can be readily expanded to irradiated ones. Both H- and D-loaded getters were studied with the goal that a comparison between the electrochemical behaviors of unloaded getters with those loaded with H or D will allow for extrapolation to those loaded with T and allow us to get predictive insight into T behavior.

Polarization Curves Obtained from Linear Sweep Voltammetry (LSV) on Unplated Getters in Aqueous Media. Initial voltammetry studies were focused on unplated getters to assess and select the electrolyte media for the controlled dissolution of the zirconium core of the getters. The electrochemical assemblies used for the voltammetry experiments are described in the Experimental Section. Linear sweep voltammetry (LSV) studies were conducted at room temperature (25 °C) on unplated Zr-4 getters of similar mass and
dimensions in a series of different electrolyte media to gain insight into the electrochemical dissolution of zirconium in different electrochemical environments, namely 1.0 M KCl in DI water, 1.0 M KBr in DI water, 1.0 M KOH in DI water, 1.0 M NaOAc in DI water, 1.0 M HNO₃ in DI water, 10% HCl/90% DI water (v/v), and conc. HCl (11.38 M). The LSVs conducted on the getters shown in Figure 2A showed near identical results to that seen for the liners seen previously, as is expected for materials of near identical compositions. Among the chosen electrolytes, alkyl halides were particularly attractive as they offer a benign media and allow electrodissolution at a voltage low enough that does not result in any interfering electrochemical reactions/ processes. 1 M KCl was adapted as the electrolyte medium for subsequent electrodissolution studies of the Zr-4 layer as it allows for a highly benign reaction condition and also due to sharper and more pronounced current drop at the onset of dissolution voltage compared to other electrolytes.

**Polarization Curves Obtained from Linear Sweep Voltammetry on Ni-Plated Getters.** Subsequently, studies were extended to Ni-plated Zr-4 getters in a set of different electrolytic media to gain insight into the electrochemical dissolution of zirconium in different electrochemical environments, namely 1.0 M KCl in DI water, 1.0 M KBr in DI water, 1.0 M KOH in DI water, 1.0 M HNO₃ in DI water, 1.0 M NaOAc in DI water, 1.0 M HNO₃ in DI water, 10% HCl/90% DI water (v/v), and conc. HCl (11.38 M). The LSvs conducted on the getters shown in Figure 2A showed near identical results to that seen for the liners seen previously, as is expected for materials of near identical compositions. Among the chosen electrolytes, alkyl halides were particularly attractive as they offer a benign media and allow electrodissolution at a voltage low enough that does not result in any interfering electrochemical reactions/processes. 1 M KCl was adapted as the electrolyte medium for subsequent electrodissolution studies of the Zr-4 layer as it allows for a highly benign reaction condition and also due to sharper and more pronounced current drop at the onset of dissolution voltage compared to other electrolytes.

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The electrochemical behavior of the Ni-plated getters was similar to the unplated getters in KCl and KBr solutions, respectively, suggesting that the Ni layer does not affect the polarization behavior of the getters in these media. Based on the near identical behavior of the Ni-plated getters with the unplated getters in these two electrolytes, the dip in current is suggestive of the dissolution of the Zr layer and not the Ni layer. However, bulk permeation of the aqueous solution through the Ni layer is unlikely due to the function of the Ni layer in preventing H₂O penetration, as described in the Introduction section. It is however possible that there may be some structural breaches in the uniformity and continuity of Ni coating in the chosen getters through which the electrolyte solutions (aqueous KCl and KBr) permeate and attack the Zr layer, causing its selective dissolution. A more careful analysis of this phenomenon is presently underway.

The polarization behavior for the Ni-plated getters is distinctly different in 1 M HNO₃ electrolyte medium compared to the unplated ones, with the LSV starting to show a dip at ~0.05 V (vs Ag/AgCl) and sharply going down at 0.1 V. This suggests that the HNO₃ solution affects the Ni layer. This can presumably be due to the following electrochemical reactions given by eqs 2–4

At cathode:

\[ \text{Ni}^{0}(s) - 2e^- = \text{Ni}^{2+}(aq) \]  

(2)

At anode:

\[ 2\text{H}^+(aq) + 2e^- = \text{H}_2(aq) \]  

(3)

Overall:

\[ \text{Ni}^{0}(s) + 2\text{H}^+(aq) = \text{Ni}^{2+}(aq) + \text{H}_2(aq) \]  

(4)

Based on the comparative study of the unplated getter, where the Zr layer was observed to be unresponsive to 1 M HNO₃ at such low oxidizing potentials, this is suggestive of a selective dissolution of the Ni layer. The polarization behavior in 1 M KOH is also different between the unplated and the Ni-plated getters. A comparison of the behavior suggests that the KOH solution attacks both the Ni and the Zr layers.

Based on these observations, HNO₃ was chosen for the removal of the Ni layer via dissolution. It was also in our interest to examine the effect of lowering the HNO₃ concentration on the electrodissolution of Ni, the aim being to try to lower chemical corrosiveness while ensuring that the required electrochemical dissolution potential is not significantly increased. Therefore, the HNO₃ concentration was progressively lowered from 1 M to 0.5 M, 0.1 M and 0.05 M, respectively (Figure 2C). It was observed that as the HNO₃ concentration was lowered, there was a progressive shift of the dipping potential to more positive values. This is consistent with the electrolyte being less oxidizing as the concentration of HNO₃ is lowered, which subsequently requires a greater voltage kick for the dissolution process. In spite of the slight increase in oxidation potentials compared to higher HNO₃ concentrations, the dissolution behavior in 0.05 M HNO₃ was

![Figure 2. Linear sweep voltammetry curves of (A) unplated getter and (B, C) Ni-plated getter vs Ag/AgCl reference electrode (ν = 100 mV/s). The electrolyte media: (a) 1.0 M KCl/DI water (lightly green), (b) 1.0 M KBr/DI water (red), (c) 1.0 M KI/DI water (light blue), (d) 1.0 M KOH/DI water (dark green), (e) 1.0 M NaOAc/DI water (light blue), (f) 1.0 M HClO₄/DI water (violet), (g) 1.0 M HNO₃/DI water (yellow), (h) conc. HCl (11.38 M) (red), (i) 0.1 M HNO₃/DI water (brown), and (k) 0.05 M HNO₃/DI water (purple). The dashed lines represent the respective blanks. Getters of near similar dimensions were used for each measurement.](https://dx.doi.org/10.1021/acsomega.0c00165)
still effective, and therefore, considering its less corrosive nature, it was chosen as a preferred electrolyte medium for the controlled potential electrolytic dissolution of the Ni layer. It should be noted that getters of similar dimensions and surface area were used for each measurement.

**Electrochemical Behavior of H/D-Loaded Getters.**

Subsequent studies involved exploring the electrochemical behavior and oxidative dissolution potential of both unplated as well as Ni-plated getters loaded with hydrogen and deuterium, which served as the nonradioactive and unirradiated surrogates of tritiated components. The aim was to establish a methodology with nonirradiated components that can be readily expanded to irradiated ones. Both H- and D-loaded getters were studied with the goal that a comparison between the electrochemical behaviors of unloaded getters with those loaded with H or D will allow for extrapolation to those loaded with T and allow us to get predictive insight into T behavior. The procedures for preparing H- or D-loaded getters are described in the Experimental Section, and the furnace is shown in the Supporting Information, Figure S1.

Three different amounts of H loadings were used, namely 1:0.2 mol Zr/H, 1:0.5 mol Zr/H, and 1:1 mol Zr/H. The linear sweep voltammograms were studied in 1 M aqueous KCl. It was observed that the dissolution potentials measured by the sharp drop in current as a function of applied voltage progressively shift to more positive voltages as the H loading is increased, as seen in Figure 3. This is a consequence of the zirconium metal center being more electron deficient in the hydrides and requiring a higher voltage kick to get oxidized.

A set of similar studies were done on the getters loaded with three different amounts of D (1:0.2 mol Zr/D, 1:0.5 mol Zr/D, and 1:1 mol Zr/D). It is observed that the behavior of D-loaded materials is similar to that of H-loaded materials, progressively shifting to more positive voltages as the D loading is increased, as seen in Figure 3, due to similar requirements of higher voltage by a more electron-deficient Zr center in the deuterides. The values for the D-loaded materials are slightly higher than those for the analogous H-loaded materials, presumably due to a kinetic isotopic effect. It is worth mentioning that the LSVs of the unplated getters are near identical to the liner materials. A similar set of studies were also done on the Ni-plated getters, both pristine as well as those loaded with varying amounts of hydride or deuteride. Unsurprisingly, the LSVs of these Ni-plated getters were also observed to show a near identical behavior to unplated getters.

**Controlled Potential Electrolysis.**

The electrochemical setup used for the electrolytic getter dissolution under controlled electrochemical potentials are described in the Experimental Section. Initially, controlled potential electrolysis (CPE) was focused on Ni-plated Zr-4 tubes for the selective and uniform radial dissolution of the Ni layer. Based on our LSV studies pointing to 0.05 M HNO₃ as an effective electrolyte medium for preferential Ni-layer dissolution, our studies focused on using this electrolyte to selectively dissolve the Ni layer. A Ni-plated getter was subjected to CPE at a fixed voltage for a specified time duration, which resulted in dissolution of Ni into the solution, visually observed by the color of the electrolyte solution gradually turning into a bluish-green color. For further validation, the electrolyte solutions post dissolution were collected, the liquid was evaporated off, and the pale blue residue was analyzed using X-ray diffraction (XRD). As shown in Figure S2, the diffractogram showed a single, highly crystalline phase consistent with Ni(NO₃)₂·6H₂O that is presumably formed during the dissolution process.

The uniformity of the dissolution process was measured by analyzing for Ni in the electrolyte solution at specific time points during the electrodissolution process using inductively coupled plasma-optical emission spectroscopy (ICP-OES). For the pristine getters not loaded with H or D, the voltage for
CPE studies was set at 100 mV vs Ag/AgCl based on the LSV studies showing that to be the region beyond which the electrodissolution process undergoes a sharp dip. Based on the linear electrodissolution observed on the unloaded getter under the above electrochemical conditions, similar conditions were employed for the dissolution of getters loaded with different amounts of hydride or deuteride. The dissolution kinetics are shown in Figure 4A,B. It is observed that the amount of H or D loading has no prominent effect on the Ni dissolution by the HNO₃ electrolyte, as demonstrated by the overlap of all the dissolution kinetic traces on top of each other and seen in Figure 4A,B.

Post dissolution of the Ni layer, focus was directed on the dissolution of the Zr-4 core. CPE was performed on the getters post Ni dissolution in 1 M KCl based on our LSV results as well as previous observations on liners. Each getter was subjected to CPE at a fixed voltage of 225 mV vs Ag/AgCl for a specified time duration, and subsequently, the uniformity of the dissolution process was estimated from the change in mass of the getter. The dissolution kinetics for the pristine getter as well as those loaded with different amounts of H or D are shown is Figure 4C. All of the getters, irrespective of the H/D loading, showed a near-linear kinetics of dissolution, suggesting the ability to control the rate and extent of dissolution using the electrochemical technique. For the pristine getter, the dissolution studies showed an initial period of dormancy, followed by a steady near-linear dissolution kinetics when measured as a function of weight fraction dissolved with time. The initial dormancy is presumably attributed to a resisting surface oxide layer and has also been observed in the case of liners in our earlier work. This initial period of dormancy progressively decreases as the level of hydride/deuteride loading increases, as observed in the almost linear dissolution kinetics from the very onset for the getters with higher amounts of hydride or deuteride.

The dissolution processes on the Zr-4 core in general were accompanied by the formation of a whitish-gray precipitate, similar to that observed for the liners. To identify the phases associated with the precipitate, they were washed repeatedly with water to dissolve any residual supporting electrolyte salt that might have been left with the solid residue and dried. The diffractograms of the residues generated from Zr-4 cores that do not have any H- or D-loading as well as the H- and D-loaded getters (namely, 1:1 mol Zr/H and 1:1 mol Zr/D) show a broad profile as shown in Figure S3, demonstrating mainly amorphous nature of the residue. The samples did show some periodic humps that may indicate some long-range orders resembling one or more ZrO₂ phases. It is worth mentioning that the list is by no means exhaustive and represents a select set of zirconia phases that can be used to fit the data. This behavior is very similar to that observed during the dissolution of the Zr-4 based liners.

As the methodology of controlled potential electrochemical dissolution allowed us to control the rate and extent of radial dissolution demonstrated by the linear dissolution-kinetic profiles, it was in our interest to utilize this technique in...
probing the radial distribution of the key elemental components in the getter. Therefore, a companion effort involved quantitative elemental analysis of the electrolyte contact solution and the generated precipitate periodically to glean insight into the dissolution kinetics of the elements. As a precursory step to this analysis, an as-received getter piece without any H-/D-loading was analyzed by ICP-OES to gain insight into the main elemental components. For this analysis, a piece of getter was dissolved in a mixture of 30% HNO₃/2% HF in DI water, and the resultant solution was analyzed. The main elemental components are given in Figure 5A. Zr, as expected, is the predominant component at 97.8%; Sn is the next dominant component at 1.7%, with Fe and Cr contributing 0.24 and 0.13%, respectively; and cobalt occurring at 0.002%. Subsequent analysis consisted of complementing the electrodissolution studies of similar getter segments with an interrogation of the contact solution and the precipitate periodically during the electrodissolution process. For this step, the getter pieces were subjected to electrodissolution for a set of different time lengths; subsequently, the piece was separated from the electrolyte solution and was washed repeatedly with DI water to separate the precipitates to the extent possible. The precipitate, electrolyte solution, and washings were dissolved in a mixture of 30% HNO₃/2% HF, made up to a desired volume and analyzed for the key elements, namely Zr, Sn, Fe, Cr, and Co. The motivation behind this analysis was to map the dissolution rate of each element and determine how the rate compares with the initial composition of the elements. The kinetic profiles for the percentage dissolution of each element when compared to its total content have shown linear correlations as shown in Figures 5B,C; further, the ratios between the slopes of these lines are near identical to the ratios of elements in the as-received getter, as shown in Table 1. This is suggestive of the elements being distributed uniformly throughout the getter bulk, and the linearity of the lines suggests that their dissolution is also uniform.

**Table 1. ICP-MS Studies on Leachate Post Getter Dissolution**

| element | % composition in getter | slope of dissolution kinetics |
|---------|-------------------------|-----------------------------|
| Zr      | 97.8                    | 0.0781                      |
| Sn      | 1.7                     | 0.0014                      |
| Fe      | 0.24                    | 0.0002                      |
| Cr      | 0.13                    | 0.0001                      |
| Co      | 0.002                   | 2.00 × 10⁻⁶                 |

**Microscopy.** A companion effort involved a complementary examination of the exposed surface of the getter through microscopic techniques. A set of electron backscatter diffraction (EBSD) mappings were collected to gain an insight into the surface microstructural chemistry of the getters post dissolution, and their changes from the starting materials. For this study, we specifically focused on getters post the removal of the nickel layer. A set of H/D-loaded getters (namely 1:1 mol Zr/H and 1:1 mol Zr/D) were ion-milled, and EBSD studies were done on the surface, as shown in Figure 6. The microscopic images in general show a series of dark islands dispersed within a lighter matrix; phase mapping was done to identify the phases and show that the darker regions mainly correspond to hydride/deuteride phases.

The phase maps of the surfaces of the getters prior to dissolution show a predominance of the respective δ-Zr-hydride/deuteride phases along with minor contributions from ε-Zr-hydride/deuteride and γ-Zr-hydride/deuteride phases as well, as shown in Table 1. Similar analysis done on the 1:1 mol Zr/D samples after 16% dissolution also shows similar phase distribution behavior predominance of the δ-Zr-deuteride phase, along with a prominent contribution from ε-Zr-deuteride and a small contribution from γ-Zr-deuteride phases as well (Figure 6 and Table 2). There is a slight gain observed in the α-Zr phase post dissolution. Similar studies were done on getters at 1:1 mol Zr/H loading post 12% dissolution, as shown in Figure S4 and Table S1. The phase distribution behavior is comparable to the undissolved getter, with a slight decrease in the amount of δ-Zr-hydride, which is compensated by a small population of the α-Zr phase. These cumulative results actually point to a lowering of the hydride/deuteride content and an increase in metallic zirconium as we probe radially into a getter core.

A closer look at surfaces using microscopy revealed an interesting feature, similar to what we had observed during the dissolution of the liners⁹ (representative 1:1 mol Zr/D shown in Figure 7; the similar figures for 1:1 mol Zr/H shown in Figure S4). The darker regions in the figures index as zirconium hydrides/deuteride, while the lighter spots index as Zr metallic phases as mentioned earlier. On the general surfaces of the H/D-loaded getters, the surfaces were characterized by a uniform coating of hydride/deuteride represented by the uniform dark regions (panels A1 and A2 in Figures 7 and S4). It is observed that as we go deeper and deeper into the material by progressively dissolving the surfaces, the hydride layers get dispersed and smaller in size (panels B, C, D 1-2 in Figures 7 and S4). This behavior mirrors our observations from the microscopic observations of H/D-loaded liners.³⁶ It suggests a funneling effect or tunneling effect of H/D migration into the getters similar to that observed for liners (schematic representation is shown in Figure 8).

**Summary.** This work describes the successful designing of an electrochemical methodology for the controlled and uniform radial dissolution of the getter components of
TPBARs, which builds on our previous demonstration technique on the controlled and uniform dissolution of liners.9,10 As observed in our previous work with liners, we demonstrated that by carefully tailoring the applied voltage and the electrochemical conditions, it is possible to control the rate and uniformity of dissolution for both pristine getters as well as H/D-loaded getters. In addition, this work illustrated that by choosing 0.05 M HNO₃ as the electrolyte medium, we could selectively dissolve the Ni layer without a effecting the Zr-4 core.

A significant achievement was that during the selective Ni removal, the rate of dissolution could still be controlled as reflected in the linearity of the Ni-dissolution rate. It is also important to note that the rate of dissolution was not influenced or affected by H/D loading. Subsequent to removal of the Ni layer, we demonstrated uniform removal of Zr-4 in a noncorrosive electrolyte solution of 1 M aqueous KCl. The uniformity of the dissolution process did not get affected by the extent of H/D loading. It is also significant that we were able to carefully expose and observe the fragile H/D-loaded pockets through controlled corrosion under uniform voltage, where the dissolution uniformity was not noticeably impacted by the surface porosities and cracks caused by the hydride/deuteride phases. The use of electrochemical voltage as the enforcer of the dissolution process allowed the flexibility to use noncorrosive salt solutions or weak acids at moderate concentrations and get away from even mildly corrosive reagents. This further assisted in dissolution uniformity by almost eliminating pure chemical dissolution steps and helping maintain the linearity of the dissolution rate. Further, the use of a highly conductive and malleable platinum foil electrode provided an efficient and uniform electrical contact with the entire surface of the getter, further helping with the linearity in the dissolution rate. This allowed for the applied voltages to be maintained at moderate values. Our studies proved that this technique can be effective in the controlled dissolution of getters generated under irradiated environments.

![Figure 7](https://example.com/image.png)

**Figure 7.** Representative secondary scanning electron microscopy (SEM) images of D-loaded getters 1:1 mol Zr/D at four different stages of dissolution examined at two magnifications: (A1−D1) 150X magnification and (A2−D2) 450X magnification. (A) As received getter, (B) 16% dissolution, (C) 37% dissolution, and (D) 56% dissolution.

| Section | Phase Color | Phase | Raw Area % | Normalized Area % |
|---------|-------------|-------|------------|-------------------|
| A2 (1:1 mol Zr:H getter post Ni removal) | Zirconium – Alpha | 1.91 | 2.5 |
| | Zirconium Hydride – Epislon | 7.49 | 9.2 |
| | Zirconium Hydride – Gamma | 10.11 | 12.0 |
| | Zirconium Hydride – Delta | 64.51 | 76.5 |
| | Zero Solutions | 15.29 | NA |
| B2 (1:1 mol Zr:D getter post Ni removal) | Zirconium – Alpha | 0.17 | 0.4 |
| | Zirconium Deuteride – Epislon | 9.22 | 19.3 |
| | Zirconium Deuteride – Gamma | 4.28 | 7.5 |
| | Zirconium Deuteride – Delta | 30.22 | 73.1 |
| | Zero Solutions | 52.08 | NA |
| C2 (1:1 mol Zr:D getter 17% Zr dissolution) | Zirconium – Alpha | 3.01 | 11.0 |
| | Zirconium Deuteride – Epislon | 3.12 | 11.6 |
| | Zirconium Deuteride – Gamma | 8.28 | 17.3 |
| | Zirconium Deuteride – Delta | 43.51 | 61.1 |
| | Zero Solutions | 42.13 | NA |

Table 2. Quantitative Distribution of Phases Observed in Figure 6

![Table 2](https://example.com/table.png)

**EXPERIMENTAL SECTION**

**Chemicals and Materials.** Potassium chloride (KCl), potassium bromide (KBr), potassium iodide (KI), potassium hydroxide (KOH) pellets, and sodium acetate (NaOAc) were obtained from Sigma-Aldrich and used without further purification. Hydrochloric acid (HCl, 95%), nitric acid (HNO₃, 70%), and ethanol (EtOH) were purchased from Fischer Scientific and used as obtained. The platinum foil and platinum wire were obtained from Sigma-Aldrich. Ag/AgCl reference electrodes were obtained from CH instruments and were soaked in 1 M KCl for 24 h before use.

The getter samples used in this work were obtained from the Salk facility at Pacific Northwest National Laboratory. For loading the samples with hydrogen/deuterium, sections of the getter with or without Ni plating were put into a quartz tube inside a tube furnace, as shown in Figure S1, which were subsequently vacuum-leak-checked to less than 0.001 torr/min. The furnace was heated to 500 °C. Hydrogen/deuterium standard leak flow was started under vacuum. Once they reached the required temperature, the valve to the vacuum
The pump was shut. Loading at 500 °C continued until the desired loading level was achieved by calculating the time required for a certain number of moles of gas to flow from the calibrated leaks. Approximate loading was confirmed by change in getter weights. The target loadings were (a) Zr/H in the molar ratios of 1:0.2, 1:0.5, and 1:1 (referred to as 1:0.2 mol Zr/H, 1:0.5 mol Zr/H, and 1:1 mol Zr/HZr/H) and (b) Zr/D in the molar ratios of 1:0.2, 1:0.5, and 1:1 (to be referred to as 1:0.2 mol Zr/D, 1:0.5 mol Zr/D, and 1:1 mol Zr/D).

**Electrochemistry.** Linear sweep voltammetry (LSV) and controlled potential electrolysis (CPE) experiments were performed using an Epsilon potentiostat (Bioanalytical Systems) with a standard three-electrode cell stand from Bioanalytical Systems. For LSV measurements, all scans were recorded on Zr-4 tubes of similar dimensions. Different kinds of working electrodes were used in contact with the Zr-4 liner to optimize electrochemical contact and reproducibility as described in the Results and Discussion section. The voltammogram scans were recorded in the presence of a Pt-wire auxiliary electrode and an Ag/AgCl reference electrode. Before running LSV on the Zr-4 liner tubes, blank voltammograms were run in the electrolyte media using the working electrode in the absence of the Zr-4 tube as the working electrode, to determine the electrochemical window for each electrolyte media. For CPE runs, an exact setup was used, the only modification being a larger surface area of the Zr-4 tube. Based on our previous studies, platinum-based foil working electrodes were chosen based on their producing the most controlled and uniform dissolution.

### Figure 8
Schematic representation of H/D migration into the liner material. The four sections represent Figure 7A1, B1, C1, and D1, respectively.

### Figure 9
Schematic representation of a working electrode assembly for the dissolution process proceeding in a Ni-plated getter (A) internally and (B) externally.

For the electro-dissolution process of the unplated getters, two different working electrode assemblies were used, in an effort to compare the effects when dissolution proceeds from the inner circumference of the getter versus when it proceeds from the outside, as described in our previous work. For the Ni-plated getters, some additional modifications were made to ensure that we were able to control the dissolution from inside or...
outside. For the instances where dissolution was desired to proceed from the internal surface, an epoxy coating was applied around the getter prior to dissolution to protect the external surface, as shown in Figure 9 (left). Likewise, for instances where dissolution was desired to proceed from the external surface, an epoxy puck was applied internally to protect the internal surface, as shown in Figure 9 (right). Post dissolution, the epoxy protection was removed by keeping the getter in contact with a solution of dichloromethane for 30–60 min. The working electrode assemblies were used in a three-electrode configuration. For all the assemblies mentioned above, it was observed that it was possible to control the rate of dissolution through careful modulation of electrochemical conditions, irrespective of whether the dissolution was attempted from inside or outside. Getters of near-identical dimensions and surface area were used for all of the electrochemical measurements to enable comparison.

**Characterization Techniques.** X-ray diffraction (XRD) patterns of the samples were recorded on a Philips XPert Multipurpose Diffractometer (MPD) (Malvern Panalytical Ltd, Malvern, UK) equipped with a fixed Cu anode operating at 45 kV and 40 mA. XRD patterns were collected in the 2θ range of 5–100° in steps of 0.04° at a rate of 5 s/step. Phase identification was performed using JADE 9.5.1 from Materials Data Inc. and the 2012 PDF4+ database from ICSD. The lattice parameters and volume-averaged crystallite sizes were calculated from whole-pattern fitting TOPAS v5 (Bruker AXS GmbH, Germany).

The solutions were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a PerkinElmer 8300DV inductively coupled plasma-optical emission spectrometer using the procedure PNNL-ESL-1CP-OES, ICP-OES Analysis (Rev. 4, 2016). High-purity calibration standards were used to generate calibration curves, and a separate standard source was used to verify continuing calibration during the analytical run. Serial dilutions were made to investigate and correct for matrix interferences. This method is similar to the EPA SW-846 Method 6010C, inductively coupled plasma-optical emission spectrometry (Rev. 3, February 2007).

X-ray photoelectron spectroscopy (XPS) data were collected in an ultrahigh vacuum chamber using a monochromated Al K X-ray source (λ = 1486.6 eV) and a GammaData/Sciencta SES-200 hemispherical analyzer. The energy resolution of the SES-200 spectrometer was approximately 0.5 eV for the reported photoemission spectra. The spectra were placed on an absolute binding energy (BE) scale by referencing the most intense C 1s peak to 285 eV. The percentages of individual elements detected were determined from the relative composition analysis of the peak areas of the bands on the basis of the relative peak areas and their corresponding sensitivity factors to provide relative compositions. Spectra were deconvoluted by fitting to pseudo-Voigt functions after subtraction of a Shirley background.

Scanning electron microscopy (SEM) was performed using an FEI Quanta 3DFEG dual-beam microscope operated at 10–20 kV. The samples were prepared by two independent methods; in the first method, the sample particles were dispersed onto a carbon tape and coated with ~5 nm of carbon to minimize charge effects. In the second method, samples were mounted on the tape and polished using typical metallographic techniques to avoid colloidal silica for polishing. Compositional analysis was performed with an Oxford 80 mm² silicon drift detector (SDD) electron dispersive spectrometry (EDS) detector. For quantitative EDS analysis, calculated K factors provided by INCA software were used. No correction for absorption within the specimen was performed. Both secondary electron images (SE) and backscatter electron images (BSE) were recorded.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/DOI/10.1021/acsomega.0c00165.

Instrumentation of the tube furnace assembly for loading the liner with specified amounts of H/D; comparison of experimental XRD patterns with those obtained from literature; representative EBSD image of the H-loaded 1:1 mol Zr/H getter after 12% electrodissolution in 1 M KCl using an electrodissolution potential of 275 mV vs Ag/AgCl; table with the quantitative distribution of phases in the representative EBSD; representative secondary electron SEM images of H-loaded liners 1:1 mol Zr/H at four different stages of dissolution (PDF)

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**Notes**
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