Dealloyed Air- and Water-Sensitive Nanoporous Metals and Metalloids for Emerging Energy Applications

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Abstract

Nanoporous metals and metalloids are a broad class of materials whose fabrication involves the selective removal of one or more sacrificial elements from a parent alloy, also known as dealloying, which produces a bulk, monolithic framework with interconnected nanoscale ligaments and pores. The first reports within this field tended to focus on precious nanoporous metals (e.g., nanoporous gold) to provide an explanation of the fundamental mechanisms that underpin conventional, aqueous solution dealloying. As the community has grown, researchers have begun to explore various non-precious metal and metalloid elements to expand the application space and versatility of nanoporous metals and metalloids. Air- and water-sensitive elements represent a particularly promising exploration for emerging energy applications - combining their chemical reactivity with the high specific surface area and unique morphology of nanoporous metals could enable significant advances in metal fuels for onboard hydrogen generation, next-generation battery electrodes, (electro)catalysts, and more. However, sensitivity to air and water imposes a significant fabrication barrier: the conventional aqueous solution dealloying approach either cannot create these materials at all, or cannot create these materials without simultaneously forming a surface oxide film, which prevents them from being used in the applications mentioned above. To mitigate this issue, the community has developed several unique dealloying strategies involving various electrochemical, liquid metal, and thermal methods. In this review, we present those novel dealloying strategies and their reaction mechanisms, provide concrete examples of their fabrication and application in energy applications, and analyze their advantages and drawbacks with a focus on recyclability, complexity, and scalability.

Keywords

Nanoporous metals, reactive metals, air-sensitive, water-sensitive, dealloying, hydrogen generation, batteries, (electro)catalysis

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1. Introduction

Bulk nanoporous metals (such as Au, Pt, Pd, Ag, Cu, Sn, Ni, Al, and Mg) and metalloids (such as Sb, B, Ge, and Si) are attractive for various applications including heterogeneous catalysis,¹⁻³ electrocatalysis,⁴⁻⁷ electrochemical energy conversion and storage,⁸⁻¹⁴ electrochemical actuators,¹⁵⁻¹⁸ sensors,^{19–21} surface-enhanced Raman scattering (SERS),^{22–24} and plasmonics.^{25–27} These bulk nanoporous metals and metalloids are typically fabricated through a selective leaching process known as dealloying, during which sacrificial atoms from a parent alloy, usually the most (electro)chemically active alloy component, spontaneously dissolve in an acidic or alkaline corroding medium,^{28–30} while atoms of the undissolved component coalesce through interfacial diffusion to form an isostructural porous network of interconnected ligaments and pores with average diameter in the nanometer range. Often, when the reduction-oxidation (redox) reaction involved in the process is not spontaneous, an external electrical voltage or current can be used to drive dissolution of the sacrificial component. In the former case (no external electrical voltage or current), the process is referred to as free corrosion dealloving.^{28–30} In the latter case (with external electrical voltage or current), the process is referred to as electrolytic dealloying.^{28–30} Free corrosion and electrolytic dealloying in aqueous solutions have been widely used for the fabrication of nanoporous metals made of precious elements such as nanoporous Au,^{31,32} Ag,^{4,33} Pt,^{34,35} Pd,^{36,37} and Cu.^{22,38} Although nanostructured metals made of precious elements are very promising for various (electro)chemical applications,^{5,18,39} precious metals are costly and therefore unsuitable for scalability. Pt, for example, is used in state-of-the-art fuel cells and metal-air batteries as the oxygen reduction reaction (ORR) electrocatalyst, 40,41 but its high cost has driven the community to search for Pt-free ORR electrocatalysts.⁴² In recent years, Earth-abundant air- and watersensitive nanostructured metals and metalloids such as Al, Mg, Zn, Fe, Si, Sb, Sn, etc., have received significant interest for their broad range of energy applications including: ignition aids for solid fuel combustion,^{43–45} active ingredients in water-powered spaceship engines such as ALICE (Aluminum ICE) rocket propellant,^{46–48} heterogeneous catalysts and electrocatalysts for fuel production (e.g., carbon dioxide reduction and water electrolysis) and for fuel consumption (e.g., oxygen reduction, hydrogen and alcohol oxidation),⁴⁹⁻⁵¹ materials for onboard and on-site hydrogen production to feed hydrogen fuel cells,^{52–54} and lithium-ion, sodium-ion, and magnesium-ion battery electrodes.^{55–58} Conventional synthesis of these Earth-abundant metals and metalloids into nanoporous metals (i.e., dealloying in aqueous media) proves difficult or impossible due to an inherent and fundamental problem: their reactive nature promotes the formation of a passive oxide film that hinders their performance in the applications discussed above. To mitigate this issue, the community has developed various alternative dealloying strategies, which will be discussed at length in this article. Alongside these novel strategies, we provide specific examples on the use of air- and water-sensitive nanoporous materials as battery electrodes, catalysts for hydrogenation of benzene, electrocatalysts for oxygen evolution and nitrogen reduction reactions, and for on-site generation of hydrogen.

Before diving into our review, we first define three selection criteria for the air- and water-sensitive elements of interest highlighted in red and green in the periodic table shown in **Figure 1**. (i) The first criterion corresponds to their reactivity with water: these are primarily elements with standard reduction potentials below 0 V versus the standard hydrogen electrode (SHE).⁵⁹ One exception is made for Sb, which has a slightly positive standard reduction potential (E_0 = +0.214 V vs. SHE for the Sb³⁺/Sb reaction).⁶⁰ Elements marked in green in this table are water-reactive but can, in principle, be fabricated in aqueous solutions with careful control over the solution's pH. These elements can also be synthesized

using the alternative dealloying strategies discussed in this article. Elements highlighted in red in the table cannot be synthesized in aqueous solutions due to their very high reactivity. (ii) The second criterion corresponds to their reactivity with air: nanostructured materials made of elements in the table in **Figure 1** are susceptible to react spontaneously with oxygen from air to form an oxide, usually through the overall reaction in **Eq. 1**:⁶¹

$$nM(s) + \frac{m}{2}O_2(g) \rightarrow M_nO_m(s) (\Delta G < 0)$$
 (Eq. 1)

In Eq. 1, M represents an element from the table in Figure 1, and n and m represent the stoichiometry in the corresponding oxide.⁶² (iii) The third criterion corresponds to their mechanical robustness for practical use: while some alkali metals like Li and Na are highly reactive with air and water, they are too ductile to preserve their mechanical stability after nanostructuring and therefore are not included in Figure 1.



Figure 1. Air- and water-sensitive elements of interest. Elements that can, in principle, be fabricated in aqueous solutions are highlighted in green; and elements that cannot be fabricated in aqueous solutions due to their very high reactivity are highlighted in red.

This comprehensive review article on nanoporous metals and metalloids for emerging energy applications is intended to be accessible to a broad audience, including non-experts in the field of dealloying. In Section 2, we start by elucidating the general chemical reaction mechanisms associated with various dealloying methods reported in literature for the fabrication of air- and water-reactive nanoporous metals and metalloids. In Section 3, we discuss various case studies alongside specific energy applications. A summary and conclusion are provided in Section 4.

2. Reaction mechanisms in dealloying

In Section 2.1, we elucidate the chemical reaction mechanisms governing the fabrication of precious nanoporous metals by free corrosion and electrolytic dealloying in aqueous solutions, taking the fabrication of nanoporous gold (NP-Au) from Au-Ag alloys as a model system. By explaining this system, we hope to introduce readers to the redox chemistry associated with dealloying, and thus help them understand the fundamental barriers associated with fabricating air- and water-sensitive nanoporous metals and metalloids. In Sections 2.2-2.8, we discuss the reaction mechanisms of recently reported alternative dealloying methods that enable creation of these air- and water-sensitive materials.

2.1. Free corrosion and electrolytic dealloying in aqueous solutions

2.1.1. Free corrosion dealloying in aqueous solutions

When a Au-Ag alloy is exposed to an appropriate corroding medium, its underlying elements (Au and Ag) are susceptible to dissolve through the following oxidation reactions, respectively:³⁰

Au (s)
$$\rightarrow$$
 Au³⁺ (aq) + 3e⁻ (E₀ = +1.50 V vs. SHE) (Eq. 2)

$$Ag(s) \rightarrow Ag^{+}(aq) + e^{-}(E_{0} = +0.80 \text{ V vs. SHE})$$
 (Eq. 3)

A voltage higher than the equilibrium potential of Au^{3+}/Au (E₀ = +1.50 V vs. SHE) is required to dissolve Au through the oxidation reaction in **Eq. 2**. Similarly, a voltage higher than the equilibrium potential of Ag⁺/Ag (E₀ = +0.80 vs. SHE) is required to dissolve Ag through the oxidation reaction in **Eq. 3**. Therefore, each of these two oxidation reactions can only proceed if it is coupled with a counter reduction reaction to supply the required voltage and consume electrons released during metal oxidation to satisfy the law of charge conservation.³⁰ In the case of free corrosion dealloying, the counter reduction potential. To further illustrate this, let us examine the free corrosion behavior of a Au-Ag parent alloy in two types of acids: non-oxidizing and oxidizing acids.

Case #1: Non-oxidizing acids. If an oxygen-free non-oxidizing acid such as 1 M of hydrochloric acid (HCl) is used for free corrosion dealloying of a Au-Ag parent alloy, the hydrogen evolution reaction (HER) given by **Eq. 4** is the reduction reaction with the highest standard reduction potential:³⁰

 $2H^+ + 2e^- \rightarrow H_2(g) (E_R = 0.0 \text{ V vs. SHE})$ (Eq. 4)

Thermodynamically, the overall redox reaction associated with free corrosion dealloying can only spontaneously proceed if the change in the Gibbs free energy is negative ($\Delta G < 0$). Since ΔG is related to both the oxidation and reduction reaction potentials through the reaction in **Eq. 5**, where q represents the overall charge transferred during the process, ΔG will be negative only if E_R - E_O is positive.

$$\Delta G = -q(E_R - E_O) \quad (Eq. 5)$$

Au can only corrode through the oxidation reaction in **Eq. 2** in combination with the HER in **Eq. 4**. Thus, for Au corrosion, $E_R-E_O = -1.50$ V, which is negative. Similarly, Ag can only corrode through the oxidation reaction in **Eq. 3** in combination with the HER in **Eq. 4**. Thus, for Ag corrosion, $E_R-E_O = -0.80$ V, which is also negative. Hence, neither Au nor Ag can dissolve in HCl, meaning that NP-Au cannot be created by free corrosion dealloying in a non-oxidizing acid. These oxidation and reduction reactions are further illustrated graphically using Evans diagrams in **Figure 2a**, where the activation polarization lines associated with Ag oxidation (solid red line) and hydrogen reduction (solid green line) do not intersect, which means that the corresponding redox reaction cannot proceed.

Case #2: Oxidizing acids. If an oxidizing acid is used, the reduction reaction with the highest standard reduction potential will proceed. For concentrated nitric acid (~15 M HNO₃), this corresponds to the reduction of nitrate ions (NO₃⁻) given by **Eq. 6**:^{29,63}

NO₃⁻ (aq) + 3H⁺ (aq) + 2e⁻ \rightarrow HNO₂ (l) + H₂O (l) (E_R = +0.93 V vs. SHE) (Eq. 6) In the case of Au oxidation through Eq. 2 in combination with the counter reduction reaction in Eq. 6, E_R-E_O = -0.57 V, which is negative, meaning that Au cannot dissolve spontaneously in concentrated HNO₃. In the case of Ag oxidation through Eq. 3 in combination with the counter reduction reaction in Eq. 6, E_R-E_O = +0.13 V, which is positive, meaning that Ag can dissolve spontaneously in concentrated HNO₃. Therefore, the maximum polarization available to drive Ag dissolution is 130 mV. Note that in practice, the effective polarization will be much lower due to reaction overpotentials (activation, charge transfer, and concentration overpotentials).³⁰ These oxidation and reduction reactions are also illustrated graphically using Evans diagrams in Figure 2b, where the activation polarization lines associated with Ag oxidation (solid red line) and NO₃⁻ reduction (solid green line) intersect, indicating that the overall redox reaction will take place spontaneously.



Figure 2. Use of Evans diagrams to explain the dissolution mechanisms of Ag in different corroding media. (a) In non-oxidizing acids, the cathodic reaction is proton reduction (solid green line), which does not intersect with Ag oxidization (solid red line), and thus Ag will not corrode. (b) In concentrated nitric acid, nitrate ion reduction (solid green line) intersects with Ag oxidation (solid red line), and Ag will corrode spontaneously.

2.1.2. Electrolytic dealloying in aqueous solutions

As discussed above in **Section 2.1.1**, NP-Au cannot be created by free corrosion dealloying of a Au-Ag parent alloy in a non-oxidizing acid (**Figure 2a**), since Ag dissolution in a non-oxidizing acid is thermodynamically unfavorable. However, NP-Au can still be created in a non-oxidizing acid (or even in neutral pH solutions⁶⁴) using electrolytic dealloying. During electrolytic dealloying, external electrical energy (applied electrical voltage or current) is used to force the dissolution of Ag using a three-electrode electrochemical cell consisting of a Au-Ag parent alloy working electrode (WE), a counter electrode (CE) commonly made of Pt foil, and a reference electrode (RE), e.g., Ag/AgCl. During selective electrolytic leaching, Ag oxidation through **Eq. 3** takes place on the Au-Ag WE when a constant potential is applied between the WE and the RE (potentiostatic dealloying), or when a constant current is applied between the WE and CE (galvanostatic dealloying). The oxidation reaction in **Eq. 3** can be coupled with one of the following reactions at the CE: the HER (**Eq. 4**), Ag deposition,⁶⁴ or ORR depending on the nature of the electrolyte as recently reported by Welborn *et al.*⁶⁵ This process results in the formation of NP-Au. The theoretical minimum required voltage can be obtained from the

potential difference of Eq. 3 and Eq. 4, namely 0.80 V as illustrated in Figure 3. In real situations, however, overpotential above this minimum required value should be applied.



Figure 3. Use of Evans diagrams to elucidate the dissolution mechanisms of Ag during electrolytic dealloying, where external electrical energy supply is required.

2.2. Air-free electrolytic dealloying in anhydrous organic electrolytes

The air-free electrolytic dealloying approach is inspired by rocking-chair battery technologies, wherein the electrolyte typically consists of a working ion (e.g., Li^+ in Li-ion batteries) dissolved in an anhydrous organic solvent.⁶⁶ The general electrochemical cell configuration for air-free electrolytic dealloying consists of a three-electrode electrochemical cell with the parent alloy in the form M_xS_{1-x} (M represents the base material, and S the sacrificial metal) used as the WE, the sacrificial metal S used as the CE and RE, and (similar to the rocking-chair battery electrolyte) an anhydrous organic solvent containing S^{z+} cations of the sacrificial element used as an S^{z+} -conducting electrolyte. A simplified cell configuration is schematized in **Figure 4** together with the following oxidation and reaction half-reactions taking place at the WE and CE, respectively:

$$S \rightarrow S^{z^+} + ze^- \qquad (Eq. 7)$$

$$S^{z^+} + ze^- \rightarrow S \qquad (Eq. 8)$$

During electrolytic dealloying, the sacrificial metal S is removed from the WE through the oxidation reaction in **Eq. 7** and plated on the CE through the reduction reaction in **Eq. 8** by either applying a constant voltage between the WE and RE (i.e., potentiostatic mode) or applying a constant current between the WE and CE (i.e., galvanostatic mode).^{9,67} In the battery community, a measure of the rate at which a battery is (dis)charged relative to its full capacity is typically referred to in terms of "C-rate" when applying a constant current. For instance, if a battery has a capacity of 1 Ah, a rate of 1C means the (dis)charge current will be 1 A, so that the battery would be fully (dis)charged in 1 hour. Since electrolyte species are not depleted, the overall air-free electrolytic dealloying concept is thus fundamentally different from conventional electrolytic dealloying in aqueous solutions, where species in the electrolyte are irreversibly reduced at the CE through HER or ORR as described in **Section 2.1**. In addition, the use of an anhydrous organic solvent electrolyte under an inert environment (i.e., air-free electrolytic dealloying) makes it possible to fabricate air- and water-sensitive nanoporous materials.^{9,67} Finally, the air-free electrolytic dealloying process makes it possible to recover the

sacrificial element on the CE through the counter reduction reaction in Eq. 8. This concept will be further discussed in Section 3.2.



Figure 4. Schematic showing a generalized air-free electrolytic dealloying process, together with halfreactions on the WE and CE. Sacrificial element S is extracted from the parent alloy M_xS_{1-x} and plated onto the CE through the external application of a voltage or current.

2.3. Vacuum thermal dealloying

Vacuum thermal dealloying relies on the difference in the partial vapor pressure of the parent alloy components: upon heating the parent alloy under vacuum, the sacrificial component (e.g., Mg or Zn) with the lower boiling point and higher partial vapor pressure is selectively removed by sublimation,^{68,69} while atoms of the component with high boiling point and lower partial vapor pressure coalesce by diffusion to form a three-dimensional bicontinuous nanoporous morphology.^{68,69} A typical vacuum thermal dealloying setup is shown in **Figure 5**.⁶⁹ The parent alloy, which is initially kept at high temperature in a sealed furnace under inert gases (i.e., argon), is exposed to low or high vacuum in order to remove the sacrificial element through sublimation.^{68,69} The condensation unit at the end allows for recovery of the sublimated sacrificial element.⁶⁹ This concept will be further discussed in **Section 3.3**.



Figure 5. Schematic of a vacuum thermal dealloying setup. The alloy in the heating furnace is kept under vacuum, allowing for sublimation of the sacrificial element, which can be recovered at the condensation unit. Reproduced from Ref. 69.

2.4. pH-controlled dealloying

pH-controlled dealloying is a form of free corrosion dealloying in which the pH of the corroding medium is adjusted to minimize the reactivity of the non-sacrificial component of an alloy. If the sacrificial and non-sacrificial components of a parent alloy are both made of non-precious elements,

both components can react with the aqueous corroding solution at different rates. However, depending on how the pH is chosen, the dissolution of the sacrificial component can occur much faster than the dissolution of the non-sacrificial component. In selecting a pH value for the corroding medium, one should investigate the system's potential-pH diagram (**Figure 6**), where the pH-dependent potential of the HER counter reduction reaction involving H^+/H_2 from **Eq. 4** (for an acidic corroding medium) or H_2O/H_2 from **Eq. 9** (for an alkaline corroding medium) is adjusted using the relation in **Eq. 10**:⁷⁰



$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \text{ (see Eq. 10 for } E_R) \quad (Eq. 9)$$

 $E_R = -59.2 \text{ mV} \times \text{pH} \quad (Eq. 10)$

Figure 6. Potential–pH diagram showing the pH-dependent reduction potential of H^+/H_2 (acid) or H_2O/H_2 (alkaline) reaction. Here, Zn will not corrode in the window highlighted in green. Reproduced from Ref. 71.

To better illustrate the principle of pH-controlled dealloying, we employ the fabrication of nanoporous Zn (NP-Zn) as an example. Here, Al is removed from a Zn-Al parent alloy to form NP-Zn by free corrosion in an aqueous corroding medium. At first glance, it may seem that fabricating NP-Zn in this way might not be possible: the standard reduction potentials of Zn and Al are -0.76 V and -1.66 V vs. SHE, respectively, and thus both elements can dissolve. If an alkaline solution with pH = 12 is used as the corroding medium, the counter reaction will be the HER in **Eq. 9**, and the corresponding reduction potential is $E_R = -0.71$ V from **Eq. 10**. At this pH, Zn can dissolve through the oxidation reaction in **Eq.** 11 in combination with the reduction reaction in **Eq. 9** since there is still a small driving force of E_R -Eo = +50 mV for Zn dissolution.⁷¹

$$Zn (s) \rightarrow Zn^{2+} (aq) + 2e^{-} (E_0 = -0.76 \text{ V vs. SHE})$$
 (Eq. 11)

However, if a pH of 14 is used instead of 12, the potential for the HER deduced from Eq. 10 will become $E_R = -0.83$ V and the driving force for Zn dissolution will become negative (i.e., $E_R-E_O = -70$ mV), meaning that Zn cannot dissolve at this pH. At pH higher than 14, Zn could dissolve through the formation of zincate ions. At pH=14 Al can dissolve through the oxidation reaction in Eq. 12 in combination with the reduction reaction in Eq. 9 because there is large driving force of $E_R-E_O = +830$ mV available for Al dissolution.⁷¹

Al (s)
$$\rightarrow$$
 Al³⁺ (aq) + 3e⁻ (E₀ = -1.66 V vs. SHE) (Eq. 12)

Thus, there is a pH window between 12.9 and 14.0 where Al can selectively dissolve without attacking Zn, as highlighted green in **Figure 6**, and this pH window is used to fabricate NP-Zn.⁷¹ This concept will be further discussed in **Section 3.4**.

2.5. Dealloying by galvanic replacement

Dealloying by galvanic replacement is another form of free corrosion dealloying in which the reduction of a metal ion, instead of a non-metal ion, drives the corrosion process. In general, two half-reactions take place during galvanic replacement: the oxidation of a metal with relatively lower reduction potential, and the reduction of a metal ion with a relatively higher reduction potential. To illustrate the general principle, we use a Cu rod immersed in a solution containing silver ions (Ag⁺) from AgNO₃, as shown in **Figure 7**.⁷² Since Cu²⁺/Cu (+0.34 V vs. SHE) has a lower standard reduction potential compared to Ag⁺/Ag (+0.80 V vs. SHE), Cu atoms on the surface of the rod will dissolve into the solution through the oxidation reaction in **Eq. 13** (**Figure 7a**):⁷²

 $Cu (s) \rightarrow Cu^{2+} (aq) + 2e^{-} (E_0 = +0.34 \text{ V vs. SHE})$ (Eq. 13)

The Cu oxidation reaction in Eq. 13 is coupled with the reduction of Ag^+ to metallic Ag through Eq. 14 (Figure 7a).⁷²

 $Ag^+(aq) + e^- \rightarrow Ag(s) (E_R = +0.80 \text{ V vs. SHE})$ (Eq. 14)

The overall driving force for the galvanic replacement reaction is therefore given by E_R - $E_O = +0.46$ V, which is positive, meaning that Cu will spontaneously dissolve. In this specific example, the initially colorless AgNO₃ solution turns blue when Cu²⁺ ions are released into the solution (**Figure 7b**).⁷² This concept has been used to create nanoporous metals as will be discussed in **Section 3.5**.



Figure 7. Illustration of galvanic replacement mechanism using a Cu rod immersed in an aqueous solution containing Ag^+ from $AgNO_3$. (a) Cu rod directly after immersion; and (b) after the reaction had proceeded for 10 min. Cu dissolves in the solution (blue color) while metallic Ag is deposited onto the rod. The inset schematics show the corresponding atomic models. Reproduced from Ref. 72.

2.6. Dealloying by reduction-induced decomposition

Reduction-induced decomposition is based on the selective dissolution of an ionic or covalent compound instead of selectively dissolving an alloy component.^{73–75} For example, nanoporous silver (NP-Ag) can be made by chemically or electrolytically reducing AgCl or Ag₂O₃ compound using a sacrificial reducing agent (in the case of chemical reduction) or a negative voltage or current (in the case of electrolytic reduction). During the chemical reduction process, the reaction proceeds uniformly on the particle surface, as shown in **Figure 8a**.⁷³ In the case of the electrolytic reduction, the reduction half-reaction taking place at the WE requires a counter oxidation half-reaction to supply electrons, meaning that a sacrificial material is oxidized at the CE. Due to the poor conductivity of the compound,

the reaction is initially restricted to the substrate/compound/electrolyte triple phase boundaries.^{73,76} The reduced metal, however, is conductive and serves as a new current collector, which moves the reaction front along the compound surface and eventually transforms the entire sample (**Figure 8b**).⁷³ This concept will be further discussed in **Section 3.6**.



Figure 8. Schematic illustration of chemically (a) and electrolytically (b) reduced Ag_2O_3 crystals. In chemical reduction (a), the reaction front propagates uniformly. In electrolytic reduction (b), the reaction front propagates from the bottom of the crystal where it is in contact with the conducting substrate. Scale bars are 2 μ m. Reproduced from Ref. 73.

2.7. Dealloying by thermal decomposition

During the fabrication of nanoporous metals by thermal decomposition, heat-induced evaporation/reduction is used to selectively remove the sacrificial component from a parent material generally consisting of a transition metal dichalcogenide or a metal salt. This thermal decomposition process generally occurs at an operating temperature of around 1000 °C under H₂ or Ar atmosphere.⁷⁷ A typical setup used in dealloying by thermal decomposition is shown in **Figure 9**.⁷⁷ The removal of the sacrificial element occurs through two parallel processes, both of which are associated with breaking covalent bonds at the gas-solid interface:⁷⁷ (i) heat-induced evaporation of the high vapor pressure chalcogen elements^{69,77} and (ii) reaction-induced removal through hydrogen gas as shown in **Eq. 15**:⁷⁷

 $MX(s) + H_2(g) \rightarrow M(s) + H_2X(g), X = S/Se \qquad (Eq. 15)$

Two key differences between thermal decomposition and the vacuum thermal dealloying method described in **Section 2.3** are: (i) the use of a non-metal, such as a chalcogen (S, Se, or Te), as the sacrificial element in thermal decomposition, while metals with low boiling point and high vapor pressures are used as sacrificial elements during vacuum thermal dealloying; (ii) the use of atmospheric pressure and a reducing gas during thermal decomposition,^{77,78} versus the vacuum conditions required in vacuum thermal dealloying. This concept will be further discussed in **Section 3.7**.



Figure 9. Schematic illustration of thermal decomposition procedure. Reproduced from Ref. 77.

2.8. Liquid metal dealloying

Liquid metal dealloying is based on the selective dissolution of sacrificial component of an alloy using a metallic melt bath as the corroding medium. This is enabled through the interplay between the enthalpies of mixing (ΔH_{mix}) of the components in the parent alloy and the metallic melt. If the component in the parent alloy has a negative enthalpy of mixing with the metallic melt element, the melt will dissolve the component. If the component in the parent alloy has a positive enthalpy of mixing with the metallic melt dissolves away the component in the parent alloy that it can more easily mix with, and leaves behind the component it cannot mix with. This is schematically illustrated in **Figure 10a-b** in the case of a Mg-Si parent alloy system in a Bi melt.^{80,81} It should be noted that a post-processing step is required to further remove the solidified metallic melt, i.e., by the use of an aqueous corroding medium, as illustrated in **Figure 10b**. This concept will be further discussed in **Section 3.8**.



Figure 10. (a) Schematic of liquid metal dealloying's working principle using the Si-Mg-Bi system. Here, the Si-Mg precursor and Bi melt were selected based on the miscibility of Mg-Bi and the immiscibility of Si-Bi. (b) Schematic of the evolution of the nanoporous structure during liquid metal dealloying. The solidified Bi melt requires an additional etching step in HNO₃, as shown in (iii). Reproduced from Ref. 81.

3. Fabrication of air- and water-sensitive nanoporous metals and metalloids

3.1. Barriers to fabrication

Unlike the precious metals described in **Section 2.1**, air- and water-sensitive materials exhibit a negative potential vs. SHE,⁷¹ giving rise to two major issues during selective leaching in aqueous solutions pertaining to their reactivity with water and air. Upon contact with water, two reactions can take place depending on the pH of the solution:

(i) in low pH solutions, these materials (i.e., both the sacrificial and non-sacrificial components) will dissolve into solution through the oxidation reaction in Eq. 16, in combination with the HER in Eq. 4^{62}

$$M(s) \rightarrow M^{z+}(aq) + ze^{-}, (E_0 < 0.0 \text{ V vs. SHE})$$
 (Eq. 16)

In Eq. 16, M, M^{z+} and z represent the material undergoing dissolution (i.e., both the sacrificial and non-sacrificial components), its corresponding ion, and its valence, respectively. This process is graphically illustrated using the Evans diagram in Figure 11a in the case of a hypothetical material with a standard reduction potential of -1.6 V vs. SHE in a pH=0 solution. Here, the activation polarization lines associated with the oxidation of the material M (solid red line) and the reduction of protons (solid green line) intersect, indicating that the overall redox reaction will spontaneously take place at low pH values. Consequently, water-reactive nanoporous materials cannot be synthesized via the common dealloying strategy in acid solutions detailed in Section 2.1. Furthermore, since the driving force for the redox reaction is proportional to ΔE (Eq. 5), the dissolution rate of the material increases as its standard reduction potential becomes more negative. In other words, water-reactive nanoporous materials are difficult to fabricate in acidic solutions as they will dissolve alongside the sacrificial component of the parent alloy, especially if their standard reduction potential is very low.

(ii) In high pH solutions, water-reactive metals can still dissolve through the oxidation reaction in **Eq. 16**, but now in combination with the reduction reaction in **Eq. 9** associated with HER in alkaline solutions. This process is also graphically illustrated using the Evans diagram in **Figure 11b** in the case of a hypothetical material with a standard reduction potential of -1.6 V vs. SHE in a pH=14 solution. Here the activation polarization lines associated with M oxidation (solid red line) and water reduction (solid green line) intersect, indicating that the overall redox reaction will spontaneously take place at high pH values. However, in this case (i.e., in high pH solutions), ions from the dissolved materials (i.e., M^{z+}) can further react with OH⁻ species to spontaneously form a hydroxide solid product (passive film) through a chemical reaction in **Eq. 17**, which blocks further dissolution of M from the parent alloy:

$M^z + zOH^- \rightarrow M(OH)_z (s) (\Delta G < 0)$ (Eq. 17)

The other major issue with this class of materials corresponds to their reactivity with air. Indeed, if exposed to air, the surface of the metal will react with oxygen to form an oxide, usually through the overall reaction in **Eq. 1**.⁶¹ For this reason, the requirement of a well-controlled environment (e.g., atmospheres of argon, nitrogen, or vacuum) limits the synthesis, handling, and storage of this class of materials.⁶² Recently, the community has developed several effective synthesis routes that help alleviate this inherent problem. In **Sections 3.2-3.8**, we aim to introduce these new strategies through concrete examples (i.e., case studies).



Figure 11. Use of Evans diagrams to elucidate the dissolution mechanism of a metal M in different corroding media including (a) acidic solutions with pH=0, and (b) alkaline solutions with pH=14. M is a hypothetical reactive metal or metalloid with a standard reduction potential of -1.6 V vs. SHE. In both cases the activation polarization lines associated with M oxidation (solid red line) and hydrogen reduction (solid green line) intersect, and therefore, M will dissolve spontaneously.

3.2. Air-free electrolytic dealloying in anhydrous organic electrolytes

3.2.1. Case study # 1: Fabrication of nearly oxide-free nanoporous aluminum for hydrogen generation by hydrolysis with pure water

3.2.1.1 Fabrication of nearly oxide-free nanoporous aluminum with recovery of sacrificial component To fabricate nanoporous Al (NP-Al), Corsi *et al.* used the cell configuration shown in Figure 12a. A bulk Al-Mg parent alloy with composition Al₃₀Mg₇₀ at. % was used as the WE, a pure Mg foil was used as the CE and RE, and 0.4 M all-phenyl complex (APC) electrolyte was used as the Mg-ion conducting electrolyte.^{9,55} A constant voltage of 450 mV vs. Mg/Mg²⁺ was applied to selectively remove Mg from the WE and plate it onto the Mg metal CE.^{9,82} After a typical dealloying time of ~45 h, the starting bulk piece of Al–Mg alloy with lateral dimensions in the centimeter range turned into brittle NP-Al (Figure 12a-b), and Mg was successfully recovered at the CE (Figure 12c).⁹ The dealloyed NP-Al exhibited the bimodal porosity shown in Figure 13, which was attributed to the presence of two phases in the parent alloy: the Mg solid solution phase and the β-Al₁₂Mg₁₇ intermetallic phase.^{9,83}



Figure 12. Schematic of the electrolytic cell setup before (a) and after (b) dealloying. During dealloying, the starting Al-Mg WE is converted into NP-Al, while the sacrificial Mg is plated onto the Mg foil CE and recovered. (c) XRD of recovered Mg. Reproduced from Ref. 9.



Figure 13. SEM images of hierarchical NP-Al under low (*a*,*b*), intermediate (*c*), and high (*d*,*e*) magnifications. Reproduced from Ref. 9.

Lee *et al.* scaled-up the fabrication protocol in Corsi *et al.* by optimizing the Mg dissolution rate through the following modifications: (i) increasing the ionic conductivity of the electrolyte by adding lithium chloride (LiCl) to APC; (ii) increasing the contact area between the WE and the electrolyte by employing a parent alloy in powder form with smaller particles; (iii) implementing a cell configuration with multiple alternating WEs and CEs, a schematic and real image of which are shown in **Figure 14a** and **Figure 14b**, respectively.⁸⁴ Following this optimization, the fabrication rate of NP-Al achieved by Lee *et al.* was reported to be twenty times higher than that of Corsi *et al.*⁸⁴ As such, Lee *et al.* used their optimized protocol to fabricate a few grams of NP-Al in powder form (**Figure 14c**), which produced H₂ by hydrolysis when added to pure water. After the reaction finished, aluminum hydroxide was left behind as the solid by-product (see **Section 3.2.1.2**), which was then converted into activated alumina (**Figure 14d**), a value-added product.



Figure 14. (a) Schematic layout of a large-scale dealloying chamber. (b) Real image of the chamber with alternating WE and CE. (c) NP-Al in powder form created by scaled-up fabrication process shown in (a) and (b). (d) Activated alumina powder converted from aluminum hydroxide co-produced with H_2 by hydrolysis of NP-Al in (c). Reproduced from Ref. 84.

3.2.1.2 Hydrogen generation by hydrolysis of nanoporous aluminum in pure water

Hydrogen (H₂) fuel is commonly generated from water by electrolysis, thermolysis, or photoelectrolysis.⁸⁵ A promising alternative method to H₂ production and storage is through metal hydrolysis, where a metal reacts with water to form H₂. The chemical reactions in **Table 1** demonstrate how H₂ can be produced using Al, Zn, and Mg metals.^{53,86–88} Hydrogen storage and transport can be achieved by sealing the metal in an inert environment until required for use, at which point it would be placed in contact with water to produce H₂. However, although such reactions are thermodynamically

favorable, in practice they are self-limiting due to the metal hydroxide layer (or metal oxide layer, depending on the conditions of their surrounding environment) that forms on the metal surface. This layer prevents water from coming into direct contact with the bare metal underneath, blocking the hydrolysis reaction from proceeding further into the bulk. Thus, these reactions are not typically observed at a neutral pH under normal temperature and pressure conditions with bulk metal materials. In high surface-area-to-volume ratio nanostructured metals, on the other hand, the structural size of the metal is on the order of its hydroxide layer thickness, which improves H₂ production yield by increasing the conversion of the pure metal into metal hydroxide.

Eq.	Chemical Reaction	Theoretical Capacity	Ref.
18	$2Al (s) + 6H_2O (l) \rightarrow 2Al(OH)_3 (s) + 3H_2 (g)$	3.7 wt. %	[9]
19	$Zn (s) + 2H_2O (l) \rightarrow Zn(OH)_2 (s) + H_2 (g)$	1.98 wt. %	[⁷¹]
20	$Mg (s) + 2H_2O (l) \rightarrow Mg(OH)_2 (s) + H_2 (g)$	3.3 wt. %	[⁸⁷]

Table 1. Hydrogen generation by metal hydrolysis in pure water

Al is particularly attractive for H₂ generation by hydrolysis due to its high natural abundance in the Earth's crust, its high theoretical gravimetric capacity for H₂ generation as shown in **Table 1**, and its abundance as secondary Al from recycled products.⁹ Corsi *et al.* and Lee *et al.* used nearly oxide-free NP-Al with ligaments between 10-20 nm as detailed in **Section 3.2.1.1**, to produce H₂ in pure water at room temperature and pressure by employing the reaction in **Eq. 18** in **Table 1**.^{9,84} The reaction yield of NP-Al was higher than other nanoporous metal hydrolysis candidates such as nanoporous magnesium (NP-Mg) and nanoporous Zn (NP-Zn) as shown in **Figure 15**.⁶² This is because NP-Al has smaller ligament sizes (~10-20 nm) compared to NP-Mg (~20-30 nm, see **Section 3.2.2.1**). On the other hand, NP-Al is fabricated in an air-free environment and thus has less surface oxide/hydroxide coverage compared to NP-Zn, which exhibits a similar ligament size versus NP-Al (see **Section 3.4.1.1**).



Figure 15. Hydrogen generation yields obtained during hydrolysis of nanoporous Al, Mg, and Zn in pure water. Reproduced from Ref. 62.

Although NP-Al is very promising as a metal fuel for on-site hydrogen generation by metal hydrolysis, there are safety concerns associated with its high pyrophoricity (**Figure 16a**).⁸⁹ In order to mitigate this issue, Lee *et al.* developed nanoporous aluminum/lithium borohydride (NP-Al/LiBH₄) composite fuel pellets with suppressed pyrophoricity, rendering NP-Al very safe to handle as shown in **Figure 16b**.⁸⁹ The authors also investigated the optimal mixing ratio between NP-Al and LiBH₄ to enhance air stability while minimizing the amount of LiBH₄ used, as shown in **Figure 17**.⁸⁹



Figure 16. (a) NP-Al/LiOH pellet and (b) NP-Al/LiBH₄ pellet after exposure to air. Reproduced from Ref. 89.



*Figure 17. Exposure of NP-Al/LiBH*⁴ *fuel pellets with different Al-to-LiBH*⁴ *ratios to air. None of the pellets caught on fire, demonstrating the suppression of the pyrophoricity of NP-Al. Reproduced from Ref. 89.*

3.2.2. Case study # 2: Fabrication of nearly oxide-free nanoporous magnesium for hydrogen generation by hydrolysis with pure water and for Li-ion battery anodes

3.2.2.1 Fabrication of nearly oxide-free nanoporous magnesium with recovery of sacrificial component A schematic of the cell configuration used by Fu *et al.* for the fabrication of NP-Mg is shown in

Figure 18a, and a picture of the actual cell shown in Figure 18c.^{62,90} It consists of a Mg-Li parent alloy with composition $Mg_{30}Li_{70}$ at. % used as the WE, pure Li metal used as the CE and RE, and 1 M lithium perchlorate (LiClO₄) in tetrahydrofuran (THF) used as the Li-ion conducting electrolyte.⁶² A constant voltage of 1.5 V vs. Li/Li⁺ was applied to selectively remove Li from the $Mg_{30}Li_{70}$ WE and plate it onto the Li metal CE, a schematic and real image of which are shown in Figure 18b and Figure 18d, respectively.⁶² After completion of dealloying, dendritic growth of Li metal was observed, marking the recovery of sacrificial Li as shown in Figure 18e.⁶² Concurrently, NP-Mg with characteristic

ligament/pore sizes in the range of 20-30 nm is created at the WE. These structure sizes were confirmed through characterization with scanning electron microscopy (SEM) and transmission electron microscopy (TEM) as shown in **Figure 19**.⁶²



Figure 18. Schematic of the electrolytic cell setup before (a) and after (b) dealloying to fabricate NP-Mg. (c) Picture of the actual cell before dealloying. (d-e) Two pictures of the actual cell showing initial Li plating at the early stage of dealloying (d), and significant Li plating when the dealloying is complete (e), which makes it possible to recover the sacrificial Li. Reproduced from Ref. 62.



Figure 19. SEM (*a-b*) and *TEM* (*c-d*) of *NP-Mg* at low and high magnifications. The characteristic ligament size is 20-30 nm. Reproduced from Ref. 62.

3.2.2.2 Hydrogen generation by hydrolysis of nanoporous magnesium in pure water

As discussed in Section 3.2.1.2, NP-Mg can be used for on-board H₂ generation when it reacts with pure water through Eq. 20 in Table 1. The H₂ generation yield is shown in Figure 15.⁶² Since NP-Mg is fabricated in an air-free environment, it exhibits a higher yield than NP-Zn (see Section 3.4.1.1) due to its lower surface oxide coverage. Compared to NP-Al, on the other hand, NP-Mg shows a lower yield as a result of its larger ligament size (20-30 nm in NP-Mg vs. 10-20 nm in NP-Al), despite similarities in their air-free fabrication protocols (see Section 3.2.1.1).

3.2.2.3 Use of nanoporous magnesium as a Li-ion battery anode

Fu *et al.* demonstrated the use of NP-Mg as a Li-ion battery (LIB) anode.⁶² For example, typical cyclic voltammograms (CVs) of NP-Mg indicate that it has a low (de)lithiation potential around 0.2 V vs. Li/Li⁺ (**Figure 20a**), which is desirable for LIB anodes. In addition, a high reversible capacity of ~1000 mAh/g was reported during (de)lithiation at a current density of 43 mA/g (**Figure 20b**). The irreversible capacity observed during the lithiation step was attributed to the formation of a solid electrolyte interphase (SEI) during the first cycle.



Figure 20. Typical cyclic voltammograms (a) and galvanostatic (de)lithiation curves at 43 mA/g (b) of NP-Mg used as a LIB anode. Reproduced from Ref. 62.

3.2.3. Case study # 3: Fabrication of nearly oxide-free nanoporous tin for Mg-ion battery anodes *3.2.3.1 Fabrication of nearly oxide-free nanoporous tin*

Yaghoobnejad *et al.* fabricated nanoporous tin (NP-Sn) *in situ* in a battery cell using a WE consisting of Mg₂Sn particles mixed with conductive carbon additives and a binder to hold the Mg₂Sn powder particles together. They used a pure Mg metal foil as the CE and RE, and 0.4 M APC as the Mg-ion conducting electrolyte.⁵⁵ A C-rate (defined in **Section 2.2**) of C/50 was applied to remove Mg from the Mg₂Sn parent alloy.⁵⁵ **Figure 21** shows a typical high magnification SEM image of a dealloyed Mg₂Sn powder particles. NP-Sn with ligament sizes in the range of 10-50 nm can be observed.⁵⁵ Similarly, Chen *et al.* reported the fabrication of NP-Sn by air-free electrolytic removal of Li from a Sn-Li parent alloy.⁹¹ The WE consists of Sn particles mixed with conductive carbon additives and a binder to hold these Sn powder particles together. Li metal was used as the CE and RE, and 1 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate/diethyl carbonate (EC/DEC) was used as the electrolyte.⁹¹ Since they started with pure Sn on the WE, a Li-rich Sn-Li parent alloy was fabricated *in situ* (inside the cell) by introducing Li into Sn (lithiation of Sn).⁹¹ The delithiation of Sn was carried out

using various current densities (i.e., at various C-rates) to create NP-Sn with tunable morphology as shown in **Figure 22**.⁹¹



Figure 21. High magnification SEM image of the dealloyed Mg_2Sn powder particles. Nanoporosity can be observed on the Sn grains as indicated by the red dashed line. Reproduced from Ref. 55.



Figure 22. SEM images showing the morphology of nanoporous Sn particles dealloyed at various C-rates from Sn-Li parent alloy particles containing 80 at. % of Li. Dealloying was carried out at the rates of (a) 10 C, (b) 1 C, (c) C/2, and (d) C/10, respectively. All scale bars are 1 µm. Reproduced from Ref. 91.

3.2.3.2 Use of nanoporous tin as a Mg-ion battery anode

Sn offers both a high theoretical capacity of 903 mAh/g and a half-cell reaction potential of ~0.15 V (vs. Mg/Mg²⁺) upon alloying with Mg to form Mg₂Sn,⁵⁵ making it a promising Mg-ion battery (MIB) anode. However, the slow reaction kinetics of Sn with Mg requires the use of nanostructured Sn. Yaghoobnejad *et al.* fabricated oxide-free NP-Sn *in situ* in a battery cell as detailed in **Section 3.2.3.1**, and further investigated its use as a MIB anode: its capacity as a function of the number of cycles at relatively fast C-rates (defined in **Section 2.2**) of C/5 and C/2 are shown in **Figure 23**. After 150 cycles, the cell cycled C/5 shows a capacity of 300 mAh/g whereas the cell cycled at C/2 shows a capacity of 150 mAh/g.⁵⁵



Figure 23. Capacity versus number of cycles (left ordinate) and corresponding Coulombic Efficiency (right ordinate) obtained at the relatively fast C-rates of C/5 (red) and C/2 (blue) on NP-Sn used as a Mg-ion battery anode. Reproduced from Ref. 55.

3.2.4. Case study # 4: Fabrication of nearly oxide-free nanoporous silicon for Mg-ion battery anodes

The WE in the cell configuration used by Zhang *et al.* for the air-free fabrication of nanoporous silicon (NP-Si) consists of Mg₂Si in the powder form, mixed with conductive carbon additives along with a binder to hold the Mg₂Si powder particles together. Pure Mg foil was used as the CE and RE, and APC as the Mg-ion conducting electrolyte.⁵⁷ A constant C-rate (defined in Section 2.2) of C/50 was used to selectively remove Mg from the WE and plate it onto the Mg metal CE. Figure 24a shows the first demagnesiation process, where sacrificial Mg is selectively removed to create NP-Si.⁵⁷ Typical SEM images of the Mg₂Si particles before and after Mg removal are shown in Figure 24b and 24c, respectively, together with energy-dispersive X-ray spectroscopy (EDS) results in the insets.⁵⁷ The signal intensity difference depicted from the insets indicates a significant amount of Mg removal from Mg₂Si after the first demagnesiation, and concurrently NP-Si with characteristic size of ~100 nm is formed (Figure 24c).⁵⁷

The high natural abundance of Si (Si is the 2nd most abundant element in the Earth's crust) and its ultrahigh theoretical gravimetric capacity for Mg storage (3816 mAh/g for the Mg₂Si phase) make Si an attractive candidate for MIB anodes.⁵⁷ However, Mg storage in Si is a diffusion-controlled process, which is extremely sluggish in bulk materials.⁵⁷ To solve this issue, Zhang *et al.* proposed using the NP-Si from **Figure 24c**, with characteristic structure size in the range of ~100 nm and with minimum surface oxide (since it is made under air-free conditions), to reversibly store Mg in the form of Mg₂Si.⁵⁷ During the demagnesiation step, its capacity reached approximately 3500 mAh/g, which corresponds to 91.7 % of Mg removed from Mg₂Si (**Figure 24a**).⁵⁷ However, subsequent attempts to electrochemically remagnesiate the NP-Si back to Mg₂Si were unsuccessful, mostly because the ~100 nm characteristic structure size in NP-Si is still too large.⁵⁷ For comparison, the characteristic structure size in NP-Si dealloyed from Mg₂Sn is ~10-50 nm as discussed in **Section 3.2.3.1**. Therefore, future efforts are needed to significantly reduce the characteristic structure size of NP-Si to enable reversible Mg storage.⁵⁷



Figure 24. (a) First demagnesiation curve of Mg₂Si electrode at a C-rate of C/50. (b-c) SEM images with EDS spectra (insets) of the Mg₂Si electrode before (b) and after (c) the first demagnesiation step. Reproduced from Ref. 57.

3.3. Vacuum thermal dealloying

3.3.1. Case study # 1: Fabrication of nanoporous transition metals

Lu *et al.* used the vacuum thermal dealloying strategy, referred to in their work as vapor phase dealloying, to fabricate nanoporous transition metals including nanoporous titanium (NP-Ti), nanoporous cobalt (NP-Co), and nanoporous nickel (NP-Ni) from Ti_2Zn_8 , Co_5Zn_{21} , Ni_2Zn_{11} parent alloys, respectively.⁶⁹ As will be discussed in **Section 4**, there is a practical limitation for the vacuum thermal dealloying method associated with fabricating homogenous parent alloys with a desired nominal stoichiometry. Since the sacrificial component has a lower melting point and higher vapor pressure, it may significantly evaporate by the time the base element with the higher melting point melts during parent alloy fabrication. To overcome this limitation, Lu *et al.* prepared their parent alloys by mechanical ball-milling followed by melt spinning to obtain thin films.⁶⁹ The typical nanoporous structure obtained after dealloying is shown in **Figure 25**, for NP-Ti (**Figure 25a**), NP-Co (**Figure 25b**), and NP-Ni (**Figure 25c**).⁶⁹ The evaporated Zn could be recovered on a glass substrate at the condenser as shown in **Figure 25d**.⁶⁹



Figure 25. Morphology of NP-Ti (a), NP-Co (b), and NP-Ni (c) after vacuum thermal dealloying at 100 Pa. (d) Photo of the recovered sacrificial Zn on a glass substrate. Reproduced from Ref. 69.

3.3.2 Case study # 2: Fabrication of nanoporous refractory metals

Similar to the fabrication of parent alloys for nanoporous transition metals discussed in Section **3.3.1**, fabrication of a parent alloy for vacuum thermal dealloying is not straightforward due to the large difference in the melting point between refractory metals and the sacrificial element. To overcome this issue, Kosmidou et al. sputtered thin film parent alloys with composition V₂₆Mg₇₄, Mo₂₅Mg₇₅, Nb₂₅Mg₇₅, and Ta₂₆Mg₇₄, which were dealloyed in the same deposition chamber.⁶⁸ The nanoporous morphologies for samples dealloyed under vacuum at 600 °C are shown in Figure 26 together with corresponding cross-sections in the insets.⁶⁸ Nanoporous vanadium (NP-V, Figure 26a) showed severe coarsening during dealloying compared to the other films due to the impact of its high homologous temperature (i.e., the temperature of a material as a fraction of its melting temperature) on surface diffusivity. In other words, since surface diffusivity is empirically correlated with homologous temperature,⁹¹ a greater degree of coarsening is observed during dealloying at high homologous temperatures.^{68,92} Film cracking was observed for nanoporous molybdenum (NP-Mo, Figure 26b) and nanoporous niobium (NP-Nb, Figure 26c), originating from misfit strains during dealloying of non-free standing samples:^{68,93} while nanoporous metals shrink during dealloying,^{82,94} the deposition substrate does not shrink, leading to tensile stresses at the interface that give rise to cracks in the films. Compared to NP-Mo, NP-Nb, and NP-V, nanoporous tantalum (NP-Ta, Figure 26d) exhibits the finest structure sizes of ~20 nm as it has the highest melting point and thus the lowest rate of surface diffusion.⁶⁸



Figure 26. SEM images of top and cross-section views (insets) of nanoporous (a) V, (b) Mo, (c) Nb, and (d) Ta thin films on Si substrates dealloyed at 600 °C under vacuum. Reproduced from Ref. 68.

3.4 pH-controlled dealloying in aqueous solutions

3.4.1. Case study # 1: Fabrication of nanoporous zinc for hydrogen generation by hydrolysis with pure water

3.4.1.1. Fabrication of nanoporous zinc

Fu *et al.* fabricated NP-Zn with a hierarchical porous architecture (**Figure 27**) using the pHcontrolled dealloying strategy to selectively remove Al from $Zn_{20}Al_{80}$ at. % parent alloy in 1 M sodium hydroxide (NaOH) solution.⁷¹ The origin of the bimodal porosity was attributed to the presence of two face-centered cubic (FCC) phases with different sacrificial Al content in the quenched $Zn_{20}Al_{80}$ parent alloy.⁷¹



Figure 27. Hierarchical NP-Zn architecture fabricated in 1 M NaOH solution. Large ligament/pore structures of 200–500 nm and small ligament/pore structures of 10–20 nm are observed. Reproduced from Ref. 71.

3.4.1.2 Hydrogen generation by hydrolysis of nanoporous zinc in pure water

As discussed in Section 3.2.1.2, NP-Zn can be used for on-board H₂ generation by reaction with pure water through Eq. 19 from Table 1. The H₂ generation yield of NP-Zn is shown in Figure 15.⁶² NP-Zn shows a lower reaction yield compared to NP-Al (see Section 3.2.1.1) and NP-Mg (see Section 3.2.2.1) due to its partial surface oxide coverage.⁷¹

3.4.2. Case study # 2: Fabrication of nanoporous cadmium

Chen *et al.* used the pH-controlled dealloying strategy to fabricate nanoporous cadmium (NP-Cd) by selective removal of Li from a Cd-Li parent alloy in a water and acetonitrile mixture (see **Figure 28**).⁹¹ Cd was not attacked because its reduction potential is higher than water reduction (-0.4 V vs. - 0.41 V).⁹¹ Relatively large ligament sizes of ~200 nm were observed and attributed to the high surface diffusivity of Cd.^{91,92,95}



Figure 28. Typical morphology of NP-Cd fabricated by selective removal of Li from Cd-Li parent alloy in a water and acetonitrile mixture. Scale bar is 2 \mum. Reproduced from Ref. 91.

3.4.3. Case study # **3**: Fabrication of nanoporous nickel and nanoporous nickel alloys as (electro)catalysts for oxygen evolution reaction and benzene hydrogenation

3.4.3.1 Fabrication of nanoporous nickel and nanoporous nickel alloys

The fabrication of NP-Ni goes back almost 100 years. In 1927, Raney nickel was fabriated by selective removal of Al from Ni-Al parent alloys in alkaline solution.⁹⁶ Due to the brittle nature of intermetallic Ni-Al compounds, this process results in powder-form Raney nickel. By using a ductile parent alloy, dealloyed NP-Ni can be prepared in bulk, monolithic form. Recently, Hakamada *et al.* demonstrated the fabrication of bulk NP-Ni via electrolytic dealloying of a rolled Ni-Mn sheet in an aqueous solution of ammonium sulfate, (NH₄)₂SO₄.⁹⁶ Detsi *et al.* reported on the fabrication of a Ni-rich nanoporous Ni alloy with a composition of Ni₆₀Fe₃₀Mn₁₀ at. %, coated with its native oxide through free-corrosion dealloying of a Mn-rich ternary alloy precursor with composition Ni₁₅Fe₂₀Mn₆₅ at. % in 1 M (NH₄)₂SO₄ aqueous solution.⁹⁷ Monolithic nanoporous Ni₆₀Fe₃₀Mn₁₀ with structural size ~10 nm and a specific surface area of ~43 m²/g was obtained from Brunauer-Emmett-Teller (BET) measurements.⁹⁷

3.4.3.2. Use of nanoporous nickel alloy as an electrocatalyst for as oxygen evolution reaction

Oxygen evolution reaction (OER) is the anodic half-reaction for water splitting. OER is critical not only for splitting water, but also as the counter reaction during CO₂ reduction into value-added

chemicals.^{28,98} A major drawback with OER electrocatalysts is their poor electrical conductivity. This is because OER favorably proceeds on non-metallic surfaces, and thus greatly increases the Ohmic overpotential, especially when the characteristic structure size is above ~100 nm.^{28,70} One strategy to solve this issue involves depositing the catalyst onto commercial Ni foams that act as both the support and the current collector.^{99–103} However, the specific surface area of commercial Ni foams, which tend to have pore sizes in the range of a few hundred µm, is significantly lower than that of dealloyed nanoporous metals with pore size in the range of a few nm.^{97,104–106} For this reason, various researchers have suggested switching to nanoporous metal electrocatalytic supports. In particular, Detsi *et al.* used the nanoporous Ni₆₀Fe₃₀Mn₁₀ discussed in **Section 3.4.3.1** coated with its native oxide as shown by the TEM image in **Figure 29a** as a robust and monolithic OER electrocatalyst.⁹⁷ Electrons generated on the native oxide coating are effectively collected by the inner nanoporous Ni₆₀Fe₃₀Mn₁₀ scaffold component.⁹⁷ The high bulk conductivity of the nanoporous Ni₆₀Fe₃₀Mn₁₀ alloy, together with its high surface area (43 m²/g by BET) and open porosity for effective mass transfer at the catalyst/electrolyte interface, enabled very high current densities during OER (**Figure 29b**) as well as extended stability.^{28,97}



Figure 29. (a) *TEM image of metal/metal-oxide electrocatalyst.* (b) *Linear sweep voltammograms obtained from the nanoporous catalyst (red) versus its dense counterpart (black). Reproduced from Ref. 97.*

3.4.3.3. Use of nanoporous nickel and nanoporous nickel alloys for hydrogenation of benzene catalysts

Since its introduction, Raney Ni has been widely used to catalyze chemical reactions on an industrial scale, including hydrogenation of adiponitrile to hexamethylenediamine, and hydrogenation of benzene to cyclohexane.¹⁰⁷ Among these reactions, hydrogenation of benzene to cyclohexane is of significant importance since the product, cyclohexane, can be further oxidized into adipic acid, a raw material used in the industrial production of polyamides such as nylon.¹⁰⁸ This process is schematically shown in **Figure 30a**. As discussed in **Section 3.4.3.1**, Raney Ni is produced through selective dissolution of Al from binary Al-Ni alloys in aqueous alkaline solutions.¹⁰⁷ Sometimes a third metal, i.e., iron, is added to Raney Ni to promote and stabilize its activity.¹⁰⁹ In recent years, efforts have been made to prepare Raney Ni with increased surface area to enhance its catalytic ability.^{110–112} Zeifert *et al.* used a mechanical alloying method to prepare a series of Al-Ni binary alloys and Al-Ni-Fe ternary alloys with fine microstructures followed by dealloying in 20 % KOH aqueous solution.¹⁰⁷ **Figure 30b** shows their benzene to cyclohexane conversion performance at 50 °C (X_A).¹⁰⁷ It can be concluded that: (i) larger surface areas (i.e., higher Al content in the precursor alloys) resulted in higher activity (conversion of benzene); (ii) the addition of Fe did not increase the activity compared to binary Al-Ni alloys, but it improved catalytic stability as shown by flat slopes in **Figure 30b**.¹⁰⁷ These results indicate

key factors such as Ni content, surface area, and addition of third metal should be considered in the development of Raney Ni for benzene hydrogenation.



Figure 30. (a) Hydrogenation of benzene. (b) Comparison of various Raney catalysts for benzene conversion to cyclohexane. Reproduced from Ref. 107.

3.4.4. Case study # 4: Fabrication of nanoporous antimony for Na-ion battery anodes

3.4.4.1 Fabrication of nanoporous antimony

Nanoporous antimony (NP-Sb) has been fabricated using various precursors and dealloying mediums. Gao *et al.* fabricated NP-Sb by selective removal of Mg from Mg₉₂Sb₈ at. % parent alloy in 2 wt. % tartaric acid.¹¹³ Liu *et al.* prepared NP-Sb by selective removal of Al from Al₃₀Sb₇₀ and Al₂₀Sb₈₀ at. % in a 20 wt. % NaOH aqueous solution at 60 °C.¹¹⁴ In this case, dealloying of Al₃₀Sb₇₀ gave rise to NP-Sb with coral-like morphology (**Figure 31a**), whereas dealloying of Al₂₀Sb₈₀ gave rise to NP-Sb with honeycomb-like morphology (**Figure 31b**).¹¹⁴ Li *et al.* fabricated NP-Sb with bimodal porosity (**Figure 32a-c**) and unimodal porosity (**Figure 32d-f**) by selective removal of Mn from Sb-Mn parent alloys with composition Sb₁₀Mn₉₀ and Sb₃₄Mn₆₆ at. % in 1 M HCl, respectively.⁵⁶



*Figure 31. SEM images of NP-Sb fabricated by selective removal of Al from Al*₃₀*Sb*₇₀ (*a*) *and Al*₂₀*Sb*₈₀ (*b*). *Reproduced from Ref. 114.*



Figure 32. (a-c) SEM images of hierarchical NP-Sb. Large ligament/pores with size between 100-300 nm and mesoscopic ligaments/pores with size \sim 10 nm can be observed. (d-f) SEM images of NP-Sb with unimodal porosity, which only exhibits mesoscopic ligament/pores with average size \sim 10 nm. Reproduced from Ref. 56.

3.4.4.2 Use of nanoporous antimony and its alloy as a Na-ion battery anode

Sb is an attractive candidate for use as a Na-ion battery (SIB) anode, considering its relatively high reversible capacity of ~550 mAh/g at practical C-rates (defined in Section 2.2), of C/2, 1C, 2C, and even higher, corresponding to ~83 % of the theoretical gravimetric capacity of the Na₃Sb phase.^{115–118} For comparison, hard carbon (a commonly-used SIB anode) exhibits a lower capacity (~350 mAh/g) and suffers from poor charge storage reversibility.^{119,120} The NP-Sb fabricated by Liu et al. through selective removal of Al from Al₃₀Sb₇₀ (see Section 3.4.4.1) showed superior rate capabilities, delivering a capacity of 420 mAh/g at a current density of 3300 mA/g.¹¹⁴ Li et al. investigated Na storage in the two types of NP-Sb discussed in Section 3.4.4.1: unimodal nanoporous Sb (UNP-Sb) and hierarchical nanoporous Sb (HNP-Sb).⁵⁶ They found that, when cycled at a C-rate of C/2, both UNP-Sb and HNP-Sb exhibit good cycling stability with a capacity retention of ~94 % after 200 cycles (Figure 33).⁵⁶ In contrast, commercial Sb exhibits rapid capacity fading within the first 20 cycles.⁵⁶ In addition, the amount of Na reversibly stored in HNP-Sb is ~27 % higher than in UNP-Sb, which is attributed to increased Na diffusion (i.e., faster mass transport) through the large pores (Figure 32) of the material.⁵⁶ Gao et al. used a series of nanoporous Sb-Bi SIB anodes with various compositions instead of pure Sb.¹¹³ Figure 34 shows the cycling performance of these nanoporous materials at a rate of 200 mA/g.¹¹³ An improved cycling stability was obtained for nanoporous Sb-Bi alloys due to the smaller volume change of Bi, along with a synergistic buffering effect with Sb.¹¹³ The optimized nanoporous Bi₂Sb₆ electrode exhibits a reversible capacity of 257.5 mAh/g after 2000 cycles (Figure 34 blue line).¹¹³



Figure 33. Capacity versus number of cycles at C/2 for NP-Sb and commercial Sb. Reproduced from Ref. 56.



Figure 34. Capacity versus number of cycles for various Sb-Bi electrodes at the current density of at 200 mA/g. Reproduced from Ref. 113.

3.4.5. Case study # 5: Fabrication of nanoporous silicon for Li-ion battery anodes

3.4.5.1. Fabrication of nanoporous silicon

To fabricate NP-Si, Tao *et al.* used a two-step dealloying process: (i) First, Al was selectively removed from Al-Si parent alloy powders with compositions $Al_{60}Si_{40}$, $Al_{80}Si_{20}$ and $Al_{90}Si_{10}$ at. % using a 2 M HCl solution.¹²¹ (ii) Then, since Al is not fully removed from the parent alloy and an oxide layer forms on Si during dealloying in HCl, the resulting nanoporous powders were washed and purified with 5 wt. % hydrofluoric acid (HF).¹²¹ This dealloying process yields spherical particles with diameters between 5-10 µm and morphology that varies with the initial concentration of Al in the parent alloy: the porosity tends to increase when Al content is increased from $Al_{60}Si_{40}$ (**Figure 35a**, **d**) to $Al_{80}Si_{20}$ (**Figure 35b**, **e**), and finally to $Al_{90}Si_{10}$ (**Figure 35c**, **f**).¹²¹



Figure 35. Typical SEM images of NP-Si etched from $Al_{60}Si_{40}$ (a, d), $Al_{80}Si_{20}$ (b, e) and $Al_{90}Si_{10}$ (c, f). Reproduced from Ref. 121.

3.4.5.2. Use of nanoporous silicon as a Li-ion battery anode

Si has an exceptionally high theoretical capacity (~4200 mAh/g) for Li storage, but suffers from significant volume changes during charge storage that leads to pulverization (cracking) of particles and causes the battery's capacity to quickly fade.¹²² Nanostructuring Si can help mitigate this pulverization issue, as Tao *et al.* demonstrated.¹²¹ The authors created NP-Si with various morphologies by controlling the composition of the parent alloy – Al₆₀Si₄₀ (Si40), Al₈₀Si₂₀ (Si20), and Al₉₀Si₁₀ (Si10) as detailed in **Section 3.4.5.1** – and investigated its performance as a LIB anode compared to micron-sized Si. **Figure 36a** shows the rate capability of these materials, where all types of porous silicon outperformed non-porous micron-sized Si.¹²¹ When cycled at a rate of 1000 mA/g, Si20 could deliver a reversible capacity of 1525 mAh/g after 100 cycles, as shown in **Figure 36b**.¹²¹ After cycling, cracks appeared in the micron-sized particles that were not present in NP-Si electrodes, suggesting that their nanoporous morphology alleviates pulverization.



Figure 36. Rate capability (a) and cycling stability (b) of chemically etched NP-Si versus micron-sized Si. Reproduced from Ref. 121.

3.4.6. Case study # 6: Fabrication of nanoporous tin for Li-ion and Na-ion battery anodes *3.4.6.1.* Fabrication of nanoporous tin

To fabricate nanoporous tin (NP-Sn), Detsi et al. selectively removed Mg from Sn₁₅Mg₈₅ at. %

using two different solutions: (i) 0.5 M acetic acid, which produced NP-Sn with a conventional nanowire morphology (**Figure 37a-b**), and (ii) 1 M (NH₄)₂SO₄, which produced NP-Sn with a hierarchical, granular morphology (**Figure 37c-e**).^{58,123}



Figure 37. Typical SEM images of (a-b) NP-Sn dealloyed in acetic acid exhibiting nanowire ligaments. (c-d) NP-Sn dealloyed in ammonium sulfate exhibiting granular ligaments. (e) TEM image showing that the primary nanograins with average size \sim 200 nm in (d) consist of \sim 5 nm subnanograins. Reproduced from Ref. 123.

3.4.6.2 Use of nanoporous tin as a Li-ion battery anode

Sn has a volumetric Li storage capacity comparable to that of Si (1991 mAh/cm³ for Sn and 2190 mAh/cm³ for Si), with the added benefit of significantly higher electrical conductivity.⁵⁸ Similar to Si, it suffers from large volume expansions (see **Section 3.4.5.2**) that cause pulverization and rapid capacity fade.^{124–126} To solve this issue, Cook *et al.* tested hierarchically porous NP-Sn powder fabricated using the method detailed in **Section 3.4.6.1** as a LIB anode.⁵⁸ Their cycling performance is shown in **Figure 38**: when cycled at a rate of 250 mA/g (0.38 C), 80 % of the maximum capacity remains (555 mAh/g) after ~300 cycles.⁵⁸



Figure 38. Capacity versus number of cycles at 250 mA/g for NP-Sn. Reproduced from Ref. 58.

3.4.6.3. Use of nanoporous tin as a Na-ion battery anode

The theoretical capacity of Sn for Na storage is 847 mAh/g,¹²³ and Detsi *et al.* achieved nearly ~ 60 % of this capacity in the initial cycles of Na-ion battery anodes made with NP-Sn. The authors

compared the performance of the two NP-Sn morphologies detailed in **Section 3.4.6.1**, and as shown in **Figure 39**, a similar initial capacity (~500 mAh/g) was achieved for both.¹²³ Granular NP-Sn shows better cycling stability than its nanowire counterpart, with a capacity retention of ~55% over 95 cycles at a rate of 40 mA/g.¹²³ Compared to other Sn-based SIB anodes, the dealloying process used to fabricate NP-Sb in this study is relatively simple and exhibits comparable cycling performance.^{127–130}



Figure 39. Capacity versus number of cycles at 40 mA/g for NP-Sn with granular shape (black) and NP-Sn with nanowire shape (red). Reproduced from Ref. 123.

3.4.7. Case study # 7: Fabrication of nanoporous boron for ammonia electrosynthesis

3.4.7.1 Fabrication of nanoporous boron

Lan *et al.* fabricated nanoporous boron (NP-B) by selective removal of the orthorhombic CoB phase from a $Co_{35}B_{65}$ at. % parent alloy using 1 M HCl.¹³¹ Figure 40 shows a typical SEM image of NP-B with average pore sizes of ~100 nm.¹³¹ The authors suggested that average pore sizes of NP-B can be tailored from 50-500 nm by tuning the phase separation process in the parent alloy.¹³¹



Figure 40. Typical SEM image of NP-B, scale bar: 200 nm. Reproduced from Ref. 131.

3.4.7.2 Use of nanoporous boron for ammonia electrosynthesis

The 100-year-old Haber-Bosch process, which converts nitrogen (N_2) into ammonia (NH_3) , underpins worldwide food production and sustains billions of human lives by providing a nitrogen source for soil fertilizers.¹³² However, this process requires high temperatures and pressures, consuming

1 % of the world's total energy production and releasing 1.4 % of global CO₂ emissions.¹³³ Discovery of a method for ammonia production that operates at room temperature and atmospheric pressure would, therefore, drastically reduce our global carbon footprint. One particularly attractive route involves reducing nitrogen electrochemically (rather than chemically) using the nitrogen reduction reaction (NRR),¹³¹ which proceeds through **Eq. 21** in acidic solutions:¹³⁴

 $N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$ (g) (0.148 V vs. reversible hydrogen electrode, RHE) (Eq. 21) As can be seen from Eq. 21, the equilibrium potential of NRR is very close to that of proton reduction (Eq. 4), thus the primary research thrust is to find an electrocatalyst that selectively promotes NRR and prohibits HER.¹³⁴ Metalloids are active catalysts for NRR under ambient conditions,^{135–137} and boron in particular stands out for its weak hydrogen adsorption and abundant valence electrons, leading to more nitrogen activation centers while effectively suppressing HER.¹³¹ Lan *et al.* fabricated NP-B (as detailed in Section 3.4.7.1) for use as NRR electrocatalysts, and tested it with the setup shown in Figure 41a. Figure 41b shows average ammonia yields and corresponding faradaic efficiencies (FEs). At -0.4 V vs. RHE, a production rate of 23.11 µg/h per milligram of electrocatalyst was achieved with a FE of 25.17 %.¹³¹ This was the highest reported NRR performance among metalloid electrocatalysts, and was comparable with state-of-the-art metal-based electrocatalysts.¹³¹



Figure 41. (a) Real image of the NRR cell setup. (b) Mass-normalized average NH_3 yield rates and corresponding Faradaic efficiencies at different reduction potentials. Reproduced from Ref. 131.

3.5 Dealloying by galvanic replacement

3.5.1. Case study: Fabrication of nanoporous aluminum

Tolbert and Detsi have patented a technology for hydrogen storage in nanostructured hydrideforming metals. Their work involves fabricating NP-Al using galvanic replacement in an atmosphere of H₂ gas, which results in a monolithic framework with two important features: an ultrafine structure size of ~10 nm, and hydride-filled pores. These frameworks can reversibly release H₂ gas, and store hydrogen in the form of metal-hydrides at low temperatures (100 °C) and at atmospheric pressure.¹³⁸

Yang *et al.* fabricated NP-Al in an ionic liquid by combining dealloying and inward-growth plating. The reaction involved in NP-Al formation is given by **Eq. 22**:^{139,140}

 $3Mg(s) + 8Al_2Cl_7 \rightarrow 2Al(s) + 3Mg^{2+} + 14AlCl_4 (Eq. 22)$

Both starting materials (Al₂Mg₃ and pure Mg) resulted in the formation of NP-Al with an average ligament size of \sim 200 nm, but with distinct morphologies. In the case of Al₂Mg₃ (Figure 42a), the removal of Mg from the parent alloy creates a porous network of Al, while Al simultaneously plates on the dealloyed framework causing continual growth of the structure (Figure 42c, top). In the case of

pure Mg (Figure 42b), the porous structure only arises from Al deposition, which results in a less interconnected and anisotropic morphology (Figure 42c, bottom).^{139,140}



Figure 42. SEM images of NP-Al prepared by galvanic replacement of Al_2Mg_3 (a) and pure Mg (b). The inset in (a) shows a histogram of the ligament size distribution. (c) Illustration of microstructure evolution during NP-Al fabrication. Reproduced from Ref. 139.

3.6 Reduction-induced decomposition

3.6.1. Case study # 1: Fabrication of nanoporous zinc for Ni-Zn battery anodes

3.6.1.1. Fabrication of nanoporous zinc

Wang *et al.* fabricated NP-Zn by chemically reducing zinc chloride (ZnCl₂) in dimethoxyethane (DME) organic solution with naphthalenide ($C_{10}H_8^-$) as the reducing agent.⁷⁴ The initially transparent ZnCl₂ sample turned black after dealloying, but did not lose its integrity, as shown on the inset of **Figure 43a**. The monolithic NP-Zn had an average ligament size of ~70 nm, as shown the SEM image in **Figure 43a**,⁷⁴ and the surface of these ligaments were covered with a 2.9 nm-thick layer of zinc oxide, as shown in the TEM image **Figure 43b**.⁷⁴



Figure 43. (a) Typical SEM image of NP-Zn with the inset showing a transparent sheet of $ZnCl_2$ turns black NP-Zn (inside the white dashed circle). (b) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of a Zn ligament covered by a layer of ZnO. Reproduced from Ref. 74.

3.6.1.2 Use of nanoporous zinc as a Ni-Zn battery anode

Zinc-based alkaline batteries (Zn metal anode versus a silver oxide, nickel oxyhydroxide, or air cathode) are one of the most promising technologies that can complement LIBs in the secondary (i.e., rechargeable) battery marketplace owing to several qualities of elemental Zn: its abundance and relatively low cost, its two-electron redox chemistry, its compatibility with aqueous electrolytes, and its high specific capacity.¹⁴¹ However, conventional Zn anodes suffer from limited cycle life and poor stability when cycled to a high depth of discharge (DoD),⁷⁴ facing issues such as morphology changes,¹⁴² passivation,¹⁴³ and dendrite formation.¹⁴⁴ Wang et al. showed that NP-Zn, with its nanoscale features and continuous Zn phase, helped mitigate some of these issues.⁷⁴ Using the reduction-induced decomposition process detailed in Section 3.6.1.1., they created a Ni-Zn battery with a NP-Zn anode, an oversized NiOOH cathode, and ZnO-saturated 6 M KOH electrolyte (Figure 44a).⁷⁴ Compared to bulk Zn powder (blue points, Figure 44b), the NP-Zn achieved both higher cyclability and capacity (green points, Figure 44b): NP-Zn delivered a capacity of ~328 mAh/g at 40 % DoD for 200 cycles, where bulk Zn only achieved $\sim 1/3$ of that capacity for ~ 25 cycles, at which point it short-circuited due to dendrite formation.⁷⁴ It should be noted that the NP-Zn structure coarsened from \sim 70 nm to \sim 500 nm during cycling as shown in the SEM image of the cycled anode in Figure 44b, presenting an opportunity for future research into stabilizing the ligaments' initial size.74



Figure 44. (a) Schematic illustration of the Ni-Zn cell. (b) Capacity versus number of cycles of NP-Zn (green) and Zn powder (blue). Inset shows SEM image of NP-Zn after 200 cycles. Reproduced from Ref. 74.

3.6.2. Case study # 2: Fabrication of nanoporous tin and lead

Chen *et al.* fabricated NP-Sn and nanoporous lead (NP-Pb) by chemically reducing SnS and PbCO₃ in 0.2 M NaBH₄ aqueous solution, respectively.⁷³ The resulting NP-Sn (**Figure 45a**) and NP-Pb (**Figure 45b**) exhibit large ligament sizes as a result of their high surface diffusivities.⁷³



Figure 45. SEM images of (a) NP-Sn and (b) NP-Pb prepared via reduction-induced decomposition of SnS and PbCO₃, respectively. Scale bars are 1 µm. Reproduced from Ref. 73.

3.7 Thermal decomposition

3.7.1. Case study # 1: Fabrication of nanoporous metals by thermal decomposition of transition metal dichalcogenides

To fabricate a variety of nanoporous transition metals, Chatterjee *et al.* employed thermal decomposition of transition metal dichalcogenides (i.e., sulfides, selenides, and mixed sulfoselenides).⁷⁷ The authors thermally decomposed NiSe₂ to form NP-Ni (**Figure 46a**), CoSe₂ to form NP-Co (**Figure 46b**), TiSe₂ to form NP-Ti (**Figure 46c**), and TaSe₂ to form NP-Ta (**Figure 46d**).⁷⁷ These nanoporous structures exhibited ligament sizes below 100 nm, despite use of elevated temperature, and the authors also found a link between the precursor crystal structure (i.e., pyrite-type vs. layered-type) and porosity evolution mechanism.⁷⁷ Specifically, in pyrite-type precursor, porosity formation resembles the traditional dealloying, while in layered-type precursor, the bicontinuous porous structure forms through aggregation of nanoscale metal clusters.^{77,145,146}



Figure 46. SEM images of nanoporous transition metals fabricated via thermal decomposition of transition metal dichalcogenides: (a) NP-Ni from NiSe₂ (scale bar: $2 \mu m$). (b) NP-Co from CoSe₂ (scale bar: $10 \mu m$). (c) NP-Ti from TiSe₂ (scale bar: 200 nm). (d) NP-Ta from TaS₂ (scale bar: 200 nm). Reproduced from Ref. 77.

3.7.2. Case study # 2: Fabrication of nanoporous metals by thermal decomposition of transition metal nitrates

In addition to metal dichalcogenides mentioned in Section 3.7.1, metal nitrates are also suitable

for thermal decomposition. Lu *et al.* reported a two-step thermal decomposition for fabricating NP-Ni and NP-Co.⁷⁸ First the nickel nitrate hexahydrate and cobalt nitrate hexahydrate precursors were heated at 100-200 °C until solidifying. Then, decomposition/reduction was conducted with H₂/Ar (5-15 vol. % H₂) reactive gas at temperatures between 250-800 °C.⁷⁸ **Figure 47** shows the typical NP-Ni structure after thermal decomposition at 300 °C, with average ligament sizes in the range of 100–200 nm.⁷⁸



Figure 47. SEM images of NP-Ni at low (a) and high (b) magnifications, fabricated using thermal decomposition at 300 °C. Reproduced from Ref. 78.

3.8 Liquid metal dealloying

3.8.1. Case study # 1: Fabrication of nanoporous magnesium

Through a two-step dealloying process, Okulov *et al.* fabricated nanoporous magnesium (NP-Mg). In the first step, the authors dealloyed a Ti(Me)Cu-based alloy (where Me can be Fe, V, Nb, or Ta) in a metallic Mg melt (see **Section 2.8** for mechanistic details) to form a multiphase system consisting of pure Mg and other non-Mg phases, as illustrated in **Figure 48a**.¹⁴⁷ In the second step, the non-Mg phases, such as hexagonal-close-packed (HCP) Ti and body-centered cubic (BCC) Ta, are etched away with 15 M HF solution (similar to the second step discussed in **Section 3.4.5.1**). Interestingly, despite rapid corrosion of Mg in acidic solutions, NP-Mg with hierarchical porosity remains after etching (**Figure 48b**) as it was protected by a 200 nm thick MgF₂ passivation film (arrows in **Figure 49**) that formed upon exposure to HF.^{147,148}



Figure 48. SEM and EDS maps showing the microstructure of the as-dealloyed $Ti_{41}Ta_9Cu_{50}$ precursor alloy before (a) and after (b) etching in 15 M HF solution. The same region is shown before and after etching to highlight the formation of hierarchically porous Mg. Reproduced from Ref. 147.



Figure 49. SEM image showing the surface passivation film (black arrows) covering the NP-Mg ligaments. Reproduced from Ref. 147.

3.8.2. Case study # 2: Fabrication of nanoporous silicon for Li-ion battery anodes

3.8.2.1. Fabrication of nanoporous silicon

Wada *et al.* fabricated NP-Si by dealloying a Mg-Si precursor with composition $Mg_{72}Si_{28}$ at. % containing Mg_2Si in an HCP-Mg matrix.^{81,149} As shown in **Figure 10**, Mg atoms are removed and replaced by Bi, resulting in the formation of a bicontinuous Si/Bi composite inside of a Bi matrix. After cooling, solid Bi is selectively removed from the composite with an aqueous solution of HNO₃, resulting in interconnected Si nanoparticles with diameters of up to 300 nm, as shown in **Figure 50a**.⁸¹ As shown in the high-resolution TEM image in **Figure 50b**, a surface oxide coats these particles, which was confirmed to be SiO₂ and SiO_x by X-ray photoelectron spectroscopy (XPS) analysis and was likely formed during HNO₃ etching.^{81,150}



Figure 50. TEM images of (a) the fabricated NP-Si and (b) surface oxide covering the NP-Si ligaments. Reproduced from Ref. 81.

3.8.2.2. Use of nanoporous silicon as a Li-ion battery anode

NP-Si created through pH-controlled dealloying showed enhanced cycling performance (see **Section 3.4.5.2**), which was attributed to a reduction in structural pulverization of Si during Li storage. A similar enhancement is also observed in the NP-Si prepared by liquid metal dealloying by Wada *et al.* (see above in **Section 3.8.2.1**).⁸¹ Considering the volume expansion of Si and the porosity of their NP-Si (60.4 %), the authors calculated that it would take a capacity of ~2000 mAh/g to completely fill in the pores during lithiation, and lithiation to a capacity higher than this would result in severe pulverization of the material.^{81,151} When cycled constantly to 1000 mAh/g (half their calculated limit), the lifetime of NP-Si electrode extended for over 1500 cycles (**Figure 51**, grey line) since the battery was operated below accommodation volume limit.⁸¹ On the other hand, when cycled at a constant current (rather than constant capacity) at 0.5 C, the NP-Si electrode shows much higher initial capacity than that of non-porous Si nanoparticles (**Figure 51**, red line vs. blue line), but exhibited faster decay compared to the constant charge capacity mode since the battery was operating above/around the accommodation volume limit.⁸¹



Figure 51. Capacity versus number of cycles for bulk 3DNP-Si (red circles) and commercial Si nanoparticles (blue circles) at 0.5C. The red dotted line is an extrapolation by exponential decay function. Gray solid circles show results in constant charge capacity mode at 1000 mAh/g. Reproduced from Ref. 81.

3.8.3. Case study # 3: Fabrication of nanoporous titanium

Wada *et al.* fabricated two nanoporous phases of Ti, namely α -Ti¹⁵² and β -Ti.¹⁵³ In the case of α -Ti, a Ti₃₀Cu₇₀ at. % parent alloy was dealloyed in a Mg melt. After submersion in HNO₃, Mg was removed and bicontinuous nanoporous α -Ti was observed with ligament diameter between 200 nm and 1 µm, depending on the temperature used (lower temperatures yield lower structure sizes). In their follow-up work, Wada *et al.* prepared nanoporous β -Ti using a mixed (Ti,Cr,Zr)-Cu parent alloy instead of Ti-Cu.¹⁵³ When comparing α -Ti and β -Ti with nearly identical porosities, it was found that the β -Ti has much higher strength and hardness as a result of its higher ligament connectivity. The follow-up

study¹⁵³ suggests using multi-component parent alloys may be the key to generating a phase inaccessible by typical pure-component parent alloys.

3.8.4. Case study # 4: Fabrication of nanoporous niobium

With a similar methodology to the examples discussed above, Kim *et al.* fabricated NP-Nb with a Ni-Nb parent alloy by dissolving Ni into a Mg melt, and then removing the solidified melt with 1 M HNO₃.^{154–156} A typical microstructure after dealloying is shown in **Figure 52** in the case of Ni₆₀Nb₄₀ at. % immersed in a Mg melt at 1123 K for 300 s.¹⁵⁵



Figure 52. Typical SEM image of the fabricated NP-Nb from Ni-Nb parent alloy immersed in Mg melt at 1123K for 300 s. The average ligament size is 233 nm. Reproduced from Ref. 155.

4. Summary and conclusion

We summarize the fabrication routes discussed in **Section 2** and **Section 3** in **Table 2**. Viewing these fabrication routes from the standpoint of environmental friendliness and cost-savings and thereby prioritizing recovery and recyclability of sacrificial elements, air-free electrolytic dealloying and vacuum thermal dealloying stand out amongst the methods discussed in this work.

Air-free electrolytic dealloying in anhydrous organic solvent electrolytes is very suitable for the production of the chemically reactive nanoporous elements highlighted in red in Figure 1. The key advantages of this method include: (i) the possibility of producing nearly oxide-free nanostructured materials despite their high chemical reactivity;⁹ (ii) scalability, as the dealloying rate can be increased by reducing the particle size in the parent materials as demonstrated by Lee *et al*:⁸⁴ (iii) a high degree of process sustainability, as the recovery of the sacrificial component at the CE improves recyclability and enables continual reuse of the dealloying electrolyte. This is clearly advantageous over conventional electrolytic dealloying, where the sacrificial element is not recovered and its dissolution contaminates the electrolyte, rendering its reuse difficult.^{9,62,84} Note that refilling the electrolyte may be necessary if volatile solvents (i.e., THF) and long dealloying times are used, but this does not impact the electrolyte salt – it can be redissolved and reused.⁸⁴ The major constraints of this method include: (i) the use of a well-controlled environment (i.e., Ar or N₂ environment with H₂O and O₂ content below 0.1 ppm) for the fabrication and storage of these reactive nanoporous materials, as well as for the storage of anhydrous chemicals (i.e., salts and organic solvents) used for the electrolyte;⁹(ii) the flammable nature of the organic solvents used in the process, if not handled and stored properly;⁵⁵ and (iii) the volatile nature of organic solvents, which need to be refilled for long dealloying times.^{55,84}

The vacuum thermal dealloying method can also be used to fabricate nearly oxide-free nanoporous materials from the reactive elements highlighted in red and green in **Figure 1**. In addition, the post-reaction condenser enables recovery of sacrificial elements, improving process sustainability.⁶⁹ Since this method only requires a high difference in vapor pressure of the underlying alloy components, a broad range of nanoporous materials can, in principle, be fabricated using this method. This means that any element, including less-noble metals and inorganic elements, can be fabricated regardless of their chemical/electrochemical reactivity and electrical conductivity, in theory.⁶⁹ In practice, however, the process requires the sacrificial element to have a high vapor pressure: so far only Zn and Mg have been employed as sacrificial elements due to this limitation.⁷⁷ More importantly, the fabrication of homogenous parent alloys with a high difference in melting point and vapor pressure is not straightforward because by the time the component with higher melting point melts, the sacrificial element with lower melting point can have already evaporated. In addition, the elevated temperatures used in this process can cause significant structural coarsening.^{68,69} Finally, this method may not be kinetically attractive for the fabrication of macroscopic bulk samples due to mass transport limitations associated with bulk diffusion.

The pH-controlled dealloying and galvanic replacement techniques are based on relatively simple working principles (i.e., spontaneous reactions) in aqueous and/or organic electrolytes. The main advantage of pH-controlled dealloying is its relative ease, as it does not require (i) the use of strong oxidizing acids used by conventional free corrosion dealloying; (ii) complicated ionic liquids used in dealloying by galvanic replacement; (iii) high temperatures used in liquid metal dealloying; (iv) an inert environment used by the air-free dealloying strategy discussed above. However, since pH-controlled dealloying takes place in a non-inert environment, the surface of nanoporous materials fabricated with this method are not oxygen-free. Instead, passive films form on their surface during dealloying, preventing their eventual use in many surface-sensitive applications (i.e., catalysis, reactive metal fuels, battery materials, etc.).⁷¹ As such, passive film formation represents the most significant drawback of pH-controlled dealloying. In addition, this process does not allow for recovery of the sacrificial element (as with any type of free corrosion dealloying), diminishing its sustainability.

Galvanic replacement, despite its relatively simple working principle, has several major constraints, including (i) the use of complicated ionic liquids; (ii) separation and recovery of metal ions from the reacted solution, which acts as a barrier towards scaling fabrication; (iii) formation (deposition) of new species on the surface of the metal framework during galvanic replacement – in other dealloying methods, the sacrificial elements dissolve in the corroding medium without further deposition.⁹ This not only enlarges the final characteristic structure size, it constrains the deposition species to be identical to the remaining metal framework for the fabrication of a pure nanoporous material.

Reduction-induced decomposition and thermal decomposition can take advantage of compound precursors instead of alloy-type precursors, and thus are not restricted by the typical drawbacks of alloy-type precursors such as melting and homogenization. The abundance of compound precursors also makes these processes flexible.⁷³ Despite this advantage, however, both methods have their drawbacks. For reduction-induced decomposition, a sacrificial reducing agent (in the case of chemical reduction) or a sacrificial reducing material on the anode side (in the case of electrolytic reduction) is required. In addition, pore size and morphology control are limited to larger pore diameters, usually >100 nm.⁷⁷ While thermal decomposition enables better control over pore size and morphology compared to reduction-induced composition (<100 nm pore diameters are possible despite high operating temperatures, which in many cases induces structural coarsening),⁷⁷ it requires the use of hydrogen gas

mixtures and forms hazardous gases such as hydrogen sulfide (H_2S) and nitrogen pentoxide (N_2O_5).^{77,78} The unsafe nature of these gases would increase the cost of safety controls in an industrial-scale thermal decomposition process, adding a significant barrier to its scalability.

Liquid metal dealloying was one of the first methods that enabled fabrication of less-noble nanoporous materials, and is suitable for scale-up fabrication owing to the utilization of top-down approaches where large alloy precursor can be used.⁸¹ However, the use of a liquid metal bath results in two significant drawbacks: (i) the high temperatures of the bath can cause severe coarsening in the dealloyed materials,⁶⁹ limiting the as-dealloyed materials' potential application space; (ii) the as-dealloyed materials are solid-liquid composites containing interconnected networks of both the desired nanoporous material (e.g., Si in the case of **Figure 10**) and liquid metal from the bath (e.g., Bi in the case of **Figure 10**). Upon removal from the bath, the liquid metal network solidifies, which imposes an additional step on the process: a post-dealloying etch in an aqueous solution (e.g., nitric acid, see **Figure 10b** step (iii)).⁸¹ This etch step brings with it the same disadvantages of pH-controlled dealloying, namely growth of passive surface oxide films and inability to recover the sacrificial element.

In this review, we introduced various fabrication methods that have enabled production of air- and water-sensitive nanoporous metals and metalloids for emerging energy applications. To contextualize these newer methods, we discussed their mechanisms following a brief background on conventional nanoporous metal fabrication by free corrosion (Section 2). Then, we expanded on these methods by providing examples of both their fabrication and their applications (Section 3). Throughout the work, we discussed advantages and drawbacks of the various methods with a focus on recyclability, complexity, and scalability, and summarized these findings in Section 4. We hope that this review can serve as an educational document to researchers both inside and outside of the dealloying community, and look forward with excitement to what the future holds for air- and water-sensitive nanoporous metals and metalloids.

Article Sections	Fabrication Routes	Elements Studied	Advantages	Drawbacks
2.2, 3.2	Air-free electrolytic dealloying	Al, Mg, Sn, Si	 Sacrificial element recovery Reuse of electrolyte Scalable synthesis 	 Use of well-controlled environment Occasional use of hazardous/volatile electrolytes
2.3, 3.3	Vacuum thermal dealloying	Ti, Co, Ni, V, Nb, Mo, Ta	 Sacrificial element recovery Applicable to elements regardless of chemical reactivity and conductivity 	 Complex design by use of high temperature and vacuum Limited sacrificial element breadth (only Zn/Mg so far)
2.4, 3.4	pH-controlled dealloying	Zn, Cd, Ni, Sb, Si, Sn, B	Relatively simple design of spontaneous reactions in aqueous solutions	 Surface oxidation Cannot recover sacrificial element

Table 2. Summary of fabrication routes

2.5, 3.5	Galvanic replacement	Al	Relatively simple design of spontaneous reactions in organic electrolytes	 Cannot recover sacrificial element Side reactions (plating)
2.6, 3.6	Reduction- induced decomposition	Zn, Sn, Pb	High abundance of compound precursor	Limited pore size and morphology control
2.7, 3.7	Thermal decomposition	Ti, Co, Ni, Ta	High abundance of compound precursor	 Use of reactive gas (H₂) Hazardous gas formation
2.8, 3.8	Liquid metal dealloying	Mg, Si, Ti, Nb	Top-down process enables mass production	 Severe structure coarsening Additional dealloying steps (see drawbacks of pH-controlled dealloying)

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Eric Detsi: Designed the structure and content of the manuscript, made Figure 1, supervised the work, and edited the manuscript. Jintao Fu: Collected all data and figures from references articles and wrote the manuscript. Samuel S. Welborn: Wrote sections of the manuscript and edited the overall manuscript.

Notes

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