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# *Electrochemical Deposition of Nanoporous Metallic Foams for Energy Applications*

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## Introduction

Nanoporous materials are characterized by the following properties such as high specific area, shape selective effects and fluid permeability. Different nanoporous materials have varying pore size (macro/meso/ micro/nano), porosity, pore size distribution, composition, and surface properties such as thermal stability, chemical stability and mechanical strength. Table 4.1 summarizes different types of porous materials and their corresponding properties and characteristics [1]. Porous metals have gained a lot of attention due to their high electrical conductivity, mechanical properties and wide application spectrum [2].

#### TABLE 4.1

	Metals	Alumino- silicate	Oxides	Polymeric	Carbon	Glass
Pore size*	Meso-	Micro-	Macro-	Meso-	Micro-	Meso-
	macro	meso	meso	Macro	meso	macro
Surface	Low	High	Medium	Low 0.6	High	Low
area/Porosity	0.1-0.7	0.3-0.7	0.3-0.6		0.3-0.6	0.3-0.6
Fluid	High	Low	Low-	Low-	Low-	High
Permeability			medium	medium	medium	
Mechanical	Strong	Weak	Weak-	Medium	Low	Strong
Strength			medium			
Thermal	High	Medium-	Medium-	Low	High	Good
stability		high	high			
Chemical	High	High	Very high	Low-	High	Medium-
stability				medium		high

Different types of nanoporous materials [1]

\* mesoporous: 2 - 50 nm, macroporous> 50 nm, microporous < 2 nm [3]

These materials have unique characteristics that underline their relevance in fields of great technological importance such as catalysis, sensors, energy harvesting and optics [3]. One subgroup of nanoporous materials is nanoporous metals (NPMs). NPMs can be synthesized by a variety of techniques such as template synthesis [4-6], surfactant mediated synthesis [7, 8], and dealloying [9]. Some of these techniques provide poor control over size and extent of porosity; furthermore, while in some methods there is control over these parameters, but only porous metals in the form of thin films can be prepared which have insufficient mechanical stability.

In other templating and fabrication methods leading to porous nanostructured materials, such as dealloying and soft/hard templating methods, it can be difficult to remove the templating media, leading to impurities in the final product. Dynamic Hydrogen Bubble Template (DHBT) Method avoids this difficulty, as the hydrogen evolved is cleanly removed from the surface. Electrodeposition by DHBT has the advantage of producing materials with shapes and morphologies not afforded by other fabrication methods, and not accessible by electrodeposition at lower overpotentials [10]. The method creates porous networked materials that can be used in a number of applications such as sensing [11-13], catalysis [14] and energy [15-16]. The porous networks provide enhanced stability while exhibiting large specific surface areas, allowing for better use of expensive noble metals.

# **Fabrication of Nanoporpous Metallic Materials**

There are many methods to produces nanoporous metallic materials, such as: dealloying technique, [17] hydrogen templating (DHBT) [3], anodization process [18], laser etching [19], combustion synthesis [6], sol–gel technique [20], nanosmelting of hybrid polymer–metal oxide aerogels [21], chemical reduction technique [22] and thermal decomposition process [23].

### Dealloying

Dealloying or selective dissolution is, among these techniques, an easy, flexible and economical strategy to produce NPMs [25]. During dealloying, the more active element is removed from a binary metallic solid solution by electrolytic dissolution, leaving behind an interconnected structure. This structure is characterized by high surface-to-volume ratio, good mechanical integrity, near-theoretical compression strength, and size-scale dependent elastic modulus [24-27]. A lot of attention has been paid to nanoporous metallic materials produced by dealloying since the important work of Erlebacher et al. [25]. This process has become the most important method to produce NPMs in the past 15 years.

Many nanoporous pure metals have been reported, such as NP–Au (figure 4.1) [26], NP–Pt, NP–Pd, NP–Ag, NP–Cu, NP–Ni (figure 4.2), NP–Co, NP–Fe, NP–Cr, NP–Mn, and NP–Ti [27-37]. Furthermore, NPMs from IIIA-VA groups, such as Ga, Sn,Bi, Pb were produced [38-40]. Nanoporous structures from semiconductor elements (Si and Ge) could also be produced [41-43]. In addition, numerous nanoporous binary, ternary, and even multicomponent alloys such as Au/Zn, Au/Cu, Au/Ag, Pt/Si, Pt/Cu, and Al/(Au,Ag,Pd) etc, were fabricated. According to Yin et al. [42] porous nanostructured germanium with interesting photoresponsive properties was synthetized from GeO<sub>2</sub> powders through an electrochemical reduction (Ge nanoparticles)–alloying (CaxGe) process in molten salt and post-zero energy-consumption water etching (dealloying).



#### FIGURE 4.1

SEM images of typical nanoporous Au morphology prepared by dealloying: (a) top view, and (b) cross-sectional view [26]



#### FIGURE 4.2

Porous Ni foam fabricated by dealloying technique [31]

#### Mechanism of Dealloying

A key aspect of any dealloying mechanism, besides the dissolution of more active component(s), is the fact that the more-noble metal atoms in the alloy must be physically removed from original lattice sites, as occupied in the non-dealloyed material, and reposition themselves on a highly porous structure during the selective dissolution. Typically, however, the driving force for atomic diffusion follows a concentration gradient or follows a direction so as to lower the overall surface area (i.e., surface energy), which clearly is not what happens during the formation of nanoporosity [43].

As illustrated in figure 4.3, the steps of dealloying are as follows:

- a) Dissolution of less noble atoms (light), leading to clustering of noble atoms (dark) on surface.
- b) Coarsening of clusters by getting more noble atoms supply until the next alloy layer is etched.
- c) Dissolution of the second layer of alloy, while the characteristic length (  $\lambda$ ) between hills remains the same;
- d) Accumulation of less noble atoms at the bases of hills,
- e) Undercutting of hills and increase in average distance between hills measured along the alloy-electrolyte interface;
- f) Nucleation of new noble atom hills as the hill-hill distance along the alloy-electrolyte distance is approximately twice the characteristic length [28].



#### FIGURE 4.3

Mechanism of porosity formation during dealloying [28] (a) Removal of less noble atoms (light) (b) Coarsening of clusters (c) Formation of Noble atom-capped hills (d) Accumulation of less noble atoms at the bases of hills (e) Undercutting of hills (f) Nucleation of new noble atoms hill

One of the first mechanisms to explain the observed enrichment of more-noble atoms on the porous skeleton was called the *Volume Diffusion model*. It was created by Pickering and Wagner [44] in the late 60s. According to this model, it was suggested that the near-surface region becomes depleted of the less-noble component. This creates a gradient perpendicular to the alloy/electrolyte interface, driving bulk diffusion of the less-noble component to the surface where it can dissolve away. This obviously creates an accumulation of the more-noble ad-atoms on the surface of the electrode due to the formation of surface vacancies created by preferential removal of the less-noble component. However, volume diffusion in the unattacked alloy was found to be quite slow; in fact, at the time this mechanism was proposed, even surface diffusion was considered too slow [43].

According to Dursun [45], the *Surface diffusion mechanism* was originally proposed by Gerischer in 1962. It involves the nucleation and growth of nuclei of the pure, or almost pure, more-noble component via a surface diffusion process. As the less-noble elements are selectively dissolved from the surface of the alloy, the remaining more-noble elements, which are in a highly disordered state, begin to reorder by surface diffusion resulting in a nucleation and growth of noble atoms-rich islands. In contrast with the *Volume Diffusion* model, this mode establishes that there is no transport of the more-active atoms to the electrode surface via volume diffusion. However, in this model, it was expected that after the initial stages of the dissolution of the less-noble element, the alloys become completely passivated, when all the surface sites are occupied by more-noble elements [45].

Following the work done by **Gerischer, Forty** *et al.* [46], the selective dissolution of the more active element should lead to the creation of surface vacancies or ad-atoms, which migrate across the surface to form pits, steps and other surface roughening features. Additionally, they can assist the migration of the residual more-noble atoms, which leads to the island growth. The coalescence of these islands by migration of the more-noble atoms exposes fresh alloy to the corrosive environment where further dissolution will occur. The main argument against this new model was also that the mechanism for sustained three-dimensional porosity development was not clear [47-48].

**Oppenheim** *et al.* [49], stated that surface diffusivities of FCC metal ad-atoms were many orders of magnitude faster in the presence of the electrolyte than in air or vacuum, exceeding the threshold value for nanoporosity formation. A minimum surface diffusion coefficient on the order of 10<sup>-14</sup> cm<sup>2</sup>

 $s^{-1}$ , was needed for the noble atoms to diffuse on the order of 1 nm in about 1 s and agree with experimental observations. It was also demonstrated that a terrace atom dissolution of silver from gold-rich alloys require a significant overpotential, which clearly agrees with the simulations [50].

**Moffat** *et al.* [51] confirmed the faster surface diffusivities of gold in an electrolyte. This model, even though it is based on simplified dissolution and diffusion rules, successfully predicts many of the aspects associated with the formation of nanoporous metals formed by dealloying, including the critical potential, parting limit, formation of unconnected porosity below Ec, etc.

Recently, **Erlebacher** [52] further developed the Monte Carlo model by introducing kinetic function to both, silver dissolution/diffusion and gold diffusion. By doing that, it was possible to simulate a "real-time" dealloying that was controlled by alloy composition and applied potential. The rates of dissolution and diffusion were based on a nearest neighbour bond-breaking model. The surface atoms were chosen at random with the dissolution/diffusional probabilities calculated for specific circumstances. The rates of dissolution and diffusion and diffusion are shown in equations 1 and 2, respectively:

$$K_{diss} = v_E \exp\left[-\frac{\alpha E_b - \phi}{K_B T}\right] \quad \text{eqn. 1}$$
  
$$K_{diff} = v_D \exp\left[\frac{\alpha E_b}{K_B T}\right] \quad \text{eqn. 2}$$

where  $\alpha$  represents the number of nearest neighbouts,  $E_b$  the bond energy, which is considered equivalent for both gold and silver and given initially as 0.15 eV, and v was the applied potential (1.75 eV).  $k_B$  and T were the Boltzmann constant and absolute temperature respectively. The was obtained after fitting experimental results of the dissolution of pure silver ( = 1x10<sup>4</sup> s<sup>-1</sup>); is an attempt of frequency of the order of the Debye frequency and set equal to 1x10<sup>13</sup> s<sup>-1</sup>. Silver dissolution rates followed the Butler-Volmer equation in the high overpotential Tafel region [25]. As illustrated in figure 4,4 [55], a model reproducing morphology of np-Au, was presented by **Erlebacher** and co-workers [52]. This model is based on three competing processes: a) the electrochemical dissolution of the less noble constituent (Ag), b) the surface diffusion of the noble constituent (Au), and c) capillary action. While the Ag atoms dissolved in a layer-by-layer mode, the gold atoms can diffuse along the surface forming islands. Further dissolution of Ag atoms leads to erosion of islands so that ligaments formed. Both temperature and presence of halides affect the mobility of the gold atoms and thus the size of islands, which are initially built by surface diffusion. For example, the tendency to form larger ligaments, when halides are added to the electrolyte during dealloying [25] or smaller ligaments are formed when the temperature is lowered.



**FIGURE 4.4** Theoretical model of gold-silver binary alloy de-alloying process [55]

#### Thermodynamics of dealloying

The difference in standard potential  $\Delta E$  of the constituents A and B is the driving force for dealloying. This driving force is described by the change of the free enthalpy  $\Delta G$  which is a function of the standard potential  $\Delta E^0$  and the molar fraction x of the particular component A and B. Other additional parameters are the universal gas constant R, the temperature T, the number of electrons transferred z and the Faraday constant F:

$$\Delta G_{A=} \Delta G_{A}^{0} - RT \ln X_{A} \ll \Delta E_{A=} \Delta E_{A}^{0} - \frac{RT}{ZF} \ln X_{A} \quad \text{eqn.3}$$
  
and  
$$\Delta G_{B=} \Delta G_{B}^{0} - RT \ln X_{B} \ll \Delta E_{B=} \Delta E_{B}^{0} - \frac{RT}{ZF} \ln X_{B} \text{ eqn. 4}$$

Accordingly, the driving force (potential  $\Delta E$ ) E dealloying =  $\Delta E_A - \Delta E_B = \Delta E_{AB} - \frac{RT}{ZF} \ln \frac{X_A}{X_P}$ 

In addition to thermodynamic considerations, two additional parameters are essential for dealloying, a) parting limit [54] and b) the critical potential [56]. The parting limit is the percentage of the more-active element below which dealloying vanishes, irrespective of how oxidizing is the potential. Only alloys of a certain range of composition can be dealloyed. For example, the fraction of Ag in the starting Au-Ag alloy has to be more than 55 at %. For lower fractions of Ag the dealloying does not proceed. For low Ag fractions within the material, the coordination by Au atoms increases. A high coordination leads to passivation of the particular atom. According to **Artymowicz** et al. [47], the coordination threshold of 9 leads to the experimentally found parting limit of about 55 at%.

egn. 5

The second parameter for dealloying is the so called **critical potential** ( $E_c$ ). This effect can be explained on the bases of the commonly known over-potential in electrochemistry. The theoretical potential as described in equ. 2 does not suffice to induce bulk corrosion. The kinetics i.e. the activation barrier for surface diffusion of the more noble Au atoms prevents corrosion throughout the bulk material. Hence, only at a certain potential (higher than the thermodynamic threshold), the current that is the dissolution of Ag atoms rapidly increases. This potential Ec depends on the composition of the starting alloy, the electrolyte, and further additives like halides [56].

Different theories based on atomistic models of dealloying were proposed. **Pickering** [56] was the first one to introduce the relation between the applied potential and the dissolution rate that characterizes the electrochemical dealloying process. From figure 4.5, at low overpotentials, relative to the critical potential  $E_c$ , the alloy displays passive-like behavior, due to the surface enrichment and blocking influence of the more-noble metal "B". This passive-like behavior results in a relatively potential-independent current with no development of bulk porosity. At a certain potential (i.e., empirical critical potential -  $E_c$ ), the current suddenly increases leading to the formation of porosity. According to Pickering [56], this dealloying behavior was classified as Type I dissolution. At this critical potential, the less-noble element(s) are dissolved and the more-noble element(s) undergo a self-organization process (i.e., by surface diffusion) producing a three-dimensional porous structure. In simple terms,  $E_c$  represents a transition between surface smoothening and severe roughening leading to bulk dealloying and porosity evolution [57-59].



FIGURE 4.5 The electrochemical behavior of binary alloys [56]

#### Coarsening of the nanoporous structure

While dealloying of a binary alloy progresses, the size of recently created pores and ligaments keeps increasing. At the same time that ligaments grow in size, more original alloy is subjected to the electrolyte allowing removal of metal atoms from the already formed ligaments, which constitutes the second stage of metal dissolution. Furthermore, even after most of the silver has been removed from the ligaments, the feature size in the structure continues to increase as long as NPG is exposed to the electrolyte thanks to the high surface self-diffusivity of gold in the electrolyte. This process is typically referred as electrochemical coarsening, post-porosity coarsening or simply coarsening. Even though coarsening happens quite fast when the material is immersed in the electrolyte, coarsening happens throughout the entire life of the material, even when it is taken out from solution.

NPG is, from the thermodynamic point of view, intrinsically unstable, i.e., its nanostructure has a very high surface energy. This instability provides the driving force behind coarsening, which is the Gibbs-Thompson effect or curvature-driven growth [57].

During coarsening, the migration of material goes from higher to lower energy sites; therefore, as smaller ligaments contribute more to the surface energy (on a per volume basis) than large ligaments, the thermodynamic driving force is larger for their elimination or incorporation into larger ligaments. As a result, the distance between adjacent ligaments increases and a significant growth of both ligaments and pore diameters was observed [58-59].

In order to rationalize the coarsening phenomenon in nanoporous metals, it was necessary to look at the growth of larger clusters at the expense of smaller clusters (typically known as Ostwald ripening). This theory was formally developed by Lifshitz and Slyozov [60] and Mullins [61] through a self-consistent mean-field theory, showing that the cluster growth asymptotically following the relation:

 $R_{av} \alpha k t^{-1/3}$  eqn 6

where  $R_{av}$  is the average cluster radius, k a proportional constant and t is the time. The number of cluster/islands was, likewise, were predicted to decrease with t<sup>-1</sup>.

A different approach considered a two-dimensional growth of static spherical-cap islands, in mass conservative systems, showing that the average radius increases with  $t^{1/4}$  [23]. Simplistically, the ripening process on an atomic level can be considered as the detachment of atoms from an island or grain boundaries, kinks and ledges; these atoms then diffuse across the metal surface as adatoms, and eventually coalescence with another island. Therefore by monitoring the change in surface area (i.e., ripening) of thermodynamically destabilized metals (i.e., gold and platinum atoms), one can determine the surface self-diffusion coefficient of metals in contact with an electrolyte. Therefore, continuing the work done by Chakraverty [62], Alonso et al. [63] and Vazquez et al. [64] developed a rounded-cap cylindrical column model that enabled the calculation of the diffusion coefficient, as shown in the following relation:

$$r^4 - r_0^4 = \frac{2\gamma a^4 D_s t}{KT} \qquad \text{eqn. 7}$$

where the average cylinder radius is given by r ( $r_0$  at t=0 is given as  $1x10^{-6}$  cm [65],  $\gamma$  is the surface tension, a is the metal lattice constant and  $D_s$  the surface self-diffusion coefficient. With this equation, a prediction of the growth of the average cylinder radius with time was possible. In addition, the following relation was derived to make this result even more useful:

$$R(t^{-1}) = \left(\frac{3zF\rho}{\pi Mq}\right) \left(\frac{2\gamma a^4 D_s t}{KT} + r_0\right)^{1/4} \qquad \text{eqn. 8}$$

Where R(t) is the surface roughness at time t and can be experimentally determined as the ratio of charge passed for the formation of an oxide monolayer between the electrodispersed state and the initial state. In equation 8, the quantity in the first parentheses represents the roughness and dimensions of the rounded-cap cylindrical columns used to approximate the surface. M is the molecular weight of the hydrous metal oxide layer (i.e.,  $Au_2O_3$ ), q is the electroreduction charge density of the oxide layer at t=0, z is the number of electrons passed per elementary reaction, F is Faraday's constant, and  $\rho$  is the density of the oxide film. Literature concerning the measurement of  $D_s$  clearly demonstrates the validity of the t<sup>1/4</sup> relationship [66].

Some of the dealloying parameters, such as temperature and the nature of the electrolyte, have been found useful in controlling pore size. Qian and Chen [53] demonstrated that ultrafine nanoporous gold, with pore size of about 5 nm, can be produced by reducing the dealloying temperature of the HNO<sub>3</sub> electrolyte from 25 °C to -20 °C. By reducing the temperature, the surface self-diffusivity of gold was decreased by approximately two orders of magnitude.

**Snyder** *et* al. [65]], showed that by dealloying Ag-Au in neutral pH silver nitrate solution, significantly smaller pores and ligaments were obtained if compared with those obtained in an acidic environment (e.g.,  $HNO_3$ ); this observation can be explained by the formation of a silver oxide layer behind the dissolution front, which reduces the post-porosity coarsening of the structure. Even though these two approaches are effective to minimize the immediate coarsening of the structure, they will not prevent coarsening of the structure once the sample is removed from the electrolyte [66].

#### The Dynamic Hydrogen Bubble Template (DHBT) Method

The 'dynamic hydrogen bubble templating' (DHBT) method can produce nanoporous structure in clean, easy and fast manner. Studies involving the deposition of structures and films using DHBT

date back to the first studies in the 1970s, however it has been used for more intense research since it was brought to the forefront by Marozzi and Chialvo [67-68]. Different single metals, including copper [82], silver [69], tin [70], gold [71], platinum [72], nickel [73], and palladium [74] can be produced by this method. It also has been applied to a number of bimetallic systems, such as CuAu [75], CuPd [76], CuAg [77], AuPt [78] AgPd and AuPd [79], NiCu [80].

As illustrated in figure 4.6, Hydrogen bubbles firstly form on the substrate and thus prevent the deposition of copper in those gaps. When gas evolution is continued, the metal ions grow between the gas bubbles. In this situation, hydrogen bubbles behave as a negative dynamic template around which the metal grows as a foam structure [81].



#### FIGURE 4.6

Hydrogen bubbling acting as template in the fabrication of a Cu foam deposited on gold substrates adapted from [81]

In electrochemistry, it is usually desirable to work within the potential window of the supporting electrolyte, be it an acid, base or ionic liquid. This is to prevent the breaking down of the electrolyte causing detrimental results when studying electrochemical processes or disruption of the growth of films. For the growth of films, electrodeposition usually occurs at less than half of the limiting current to avoid unstable formations or protrusions, such as dendrites [82].

The DHBT method, however, involves working at extreme overpotential that forces the electrolyte, usually an aqueous solution containing acid, to break down and evolve hydrogen bubbles that serve to shape and form films with porous, high surface areas. Due to the large overpotential utilized, a co-reduction process occurs where metal ions in the electrolyte are reduced at the same time as  $H^+$ , a process where equations 9 and 10 occur simultaneously.

$M^{n+}(aq)+ne-\rightleftharpoons M(s)$	eqn. 9
$2H^+(aq)+2e-\rightleftharpoons H_2(g)$	eqn. 10

Hydrogen ions supplied by the supporting electrolyte are reduced to form micro-bubbles on the electrode surface. Bubble formation on an electrode surface occurs in three key steps: nucleation, growth and detachment [83]. Due to the high overpotential used by DHBT, super saturation of  $H_2$  in the solution near the electrode causes heterogeneous nucleation of bubbles at the surface. Small bubbles coalesce to form larger bubbles and continue to grow, as long as they are attached to the surface, until they reach a critical size, known as the 'bubble break-off diameter'. The break off

diameter was related to the ability of a bubble to coalesce and its residence time on the surface. These factors are dependent on the surface energy and morphology of the surface at which reduction is taking place on [84-86]

The bubbles attached to and detaching from the surface of the electrode disrupt the surface, affecting the subsequent co-reduction of metal ions from the same electrolyte. The role of these bubbles are critical, and their behaviour directly affects the metal deposition. Hydrogen bubbles insulate and block surface sites on the substrate, which would otherwise be available for reduction of incoming metal ions, forcing the ions to seek out sites around the bubbles [86].

At a critical size, the bubble breaks away from its occupancy site on the electrode surface, leaving behind a void. The growing metal surface will thus have to grow around these bubbles, which act as a dynamic template. Depositing for longer times usually results in an increase in the size and thickness of the metal film, with relatively small pore sizes at the surface of the film, which gradually increase in a 'stack up' model approach, as shown schematically in figure 4.7 [87].



#### FIGURE 4.7

Schematic of the Dynamic Hydrogen Bubble Templating Method [87]

As illustrated in table 4.2, the  $J^0$  values indicated a significantly faster H<sub>2</sub> evolution rate off the electrodepositing Pt or Pd compared to either Cu or Au. A faster rate means shorter residence times of bubbles on the surface, leading to a smaller break off diameter, reducing the amount of time available for coalescences to occur. Less time for coalescence means smaller bubbles are formed, that are directly linked to pore size in the final deposit [88].

#### TABLE 4.2

The exchange current density, j<sup>0</sup>, or the rate of hydrogen evolution/unit area for different metals [88]

Metal	Exchange Current Density, A cm <sup>-2</sup>
Au	10 <sup>-5.4</sup>
Cu	10 <sup>-5.37</sup>
Pd	10 <sup>-3</sup>
Pt	10 <sup>-3.1</sup>

Natural convection of species to an electrode occurs in any electrodeposition process, which causes the formation of a diffusion layer. Fick's second law predicts that thickness of the diffusion layer

increases relative to time, however by stirring the solution the thickness of diffusion layer is reduced [82].

According to J. Niu et al [90], the nucleation rate "w" induced by electrochemical deposition, can be expressed from the following formula:

$$w = k_1 e^{-\left[\frac{k_2}{\eta_k^2}\right]}$$
 eqn. 11

where  $k_1$ ,  $k_2$  are constants,  $\eta_k$  is the over potential.

The relation between the critical nucleation radius " $r_c$ " and the over potential " $\eta_k$ " can be calculated using the following equation:

$$r_c = rac{\pi h^3 E}{6Z_e \eta_k}$$
 eqn. 12

where E is interfacial energy, Z is the electron number of discharge ions, h is the height formed by absorbent atoms. According to the above equations, as the over potential and nucleation rate increase the nucleation rate increases and critical nucleation radius decreases, which is preferred to the formation and refinement of the initial grain. On the other hand, the hydrogen bubbles evolution rate of gradually increases with increasing the current density, which producing much larger driving force for  $H_2$  bubbles to deviate from the cathode metal foil. Consequently, the crystal growth time will be reduced, leading to the refinement of porous metal grain [82].

Generally, as stated by **J. Niu** et al [90], the characteristics of porous structures are dependent on many factors; a) the metal being deposited, b) the composition of the electrolyte c) overpotential applied d) current density, and f) temperature. Different dynamic template, can be obtained by adjusting the current density, since the evolution rate of hydrogen bubbles is closely related to the deposition current.

The morphology of metal foams, can be changed from distributed sparse dendrites to honeycomblike structure with increasing the deposition current density. Further increasing the current density could lead to the grain refinement and lattice parameter reduction. At low current density, few  $H_2$ bubbles can evolve from the surface of metal substrate, therefore, producing many available deposition areas on the cathode foil, making it difficult for metal ions to form interconnected porous structure. This is the reason why the scattered and irregular morphology of porous films appear on the surface of cathode. With increasing current density, abundant hydrogen bubbles formed and clustered, which inhibited the growth of metal atoms towards the hydrogen bubbles, making the electrochemical reaction only occurs at the interstices of hydrogen bubbles. This will lead to electrodeposition of the porous structure.

At constant current density, increasing the reaction temperature will lead to more hydrogen bubbles formation, resulting in the enhancement of the hydrogen evolution and the formation of larger bubble templates and larger pore size. Meanwhile, high temperature provides more activation for metal ions to deposit, resulting in grain coarsening of the dendrites [90].

Figure 4.8 shows a schematic diagram for the possible formation of fern-shaped dendrites during electrodeposition of Zinc, obtained by Hsu et al [91]. Once an existing dendrite is surrounded by a couple of hydrogen bubbles, the concentration of zinc ions can be divided into two zones, i) a  $Zn^{2+}$  depleted zone in the space between the two bubbles and ii) a zone with the original  $Zn^{2+}$  concentration outside them. The  $Zn^{2+}$  concentration difference between these two zones can cause local convection, replenishing the zinc ions necessary for the growth of the main stem of the fern-shaped dendrites. The formation of hydrogen bubbles suppresses the lateral growth of fern-shaped dendrites, while a fast tip growth, is enhanced by the highly concentrated electric field. When the

main stem outgrows the surrounding hydrogen bubbles, its side branches start to split, leading to the appearance of fern-shaped dendrites [91].



#### FIGURE 4.8

Formation mechanism of fern-shaped dendrites. a) Circles indicate hydrogen bubbles. b) The dotted arrowhead lines indicate the electric field. c) , d) The main stem of the fern-shaped dendrite grows between two hydrogen bubbles [91]

#### **Combustion Synthesis**

Combustion synthesis or the called self-propagating high-temperature synthesis or SHS, refers to techniques that utilize decomposition of energetic substances to produce materials. In these techniques, the inherent energy released from combustion of the precursor mixture drives forward reactions with high activation energy barriers at room temperature [20]. Nanoporous metal foams can be prepared by ignition of high nitrogen transition metal complexes. This combustion synthesis technique is a flexible general approach for the production of a wide range of nanoporous metallic foams such as Fe, Co, Ni, Cu, Zn, Pd, Ag, Pt, Au. In addition, nanoporous binary metal oxides, ceramics, and intermetallics systems can be produced, such as Pt<sub>3</sub>Ru<sub>2</sub>, Co<sub>2</sub>Pt<sub>3</sub>, CoPt, Co<sub>2</sub>Pt, IrPt, Rh<sub>2</sub>Ru, Rh<sub>3</sub>Ru<sub>2</sub>, RhRu, Ir<sub>2</sub>Ru, IrRu [20, 92].

## **Applications of NMFs**

Porous nanostructured materials are attractive materials for use in many catalytic [93], gas-sensing [94], optical [95], and mechanical applications [96]. This is due to high surface area, ultralow density, and high strength-to-weight ratio. In addition to the important characteristic of metals, such as good electrical and thermal conductivity, selected catalytic activity, and malleability, resulting in its wide range applications for acoustical insulation, electromagnetic shielding, fuel cell, and plasmatic resonance [97].

#### Viable Hydrogen Production and Storage

Hydrogen is a clean and fully recyclable substance with a practically unlimited supply. Thus, it is considered an ideal energy carrier that can be an alternative to fossil fuels. The electrochemical hydrogen production by alkaline water splitting is one of most economic environmentally friendly techniques. However, there is a limit in its large scales production due to high-energy consumption of alkaline water electrolyzes process [98-101].

Herraiz-Cardona et al [101] stated that although platinum shows the highest activity for the hydrogen evolution reaction (HER), new electrode materials have been synthetized, aiming at minimizing the cost associated with the electrocatalyst development. Among these materials,

nickel and Ni-based alloys have a high initial electrocatalytic activity toward the HER. The electrode activity, can be improved by enlarging the real surface area and/or the intrinsic activity of the electrode material. It is possible to produce a porous three-dimensional (3D) structure with a high surface roughness factor  $R_f$ , by several techniques such as electrodeposition or thermal spray depositing Ni together with an active metal like Al or Zn, followed by the dissolution of the secondary component (Raney type electrodes). Another possible technique is electrodeposition of Ni with controlled porosities and layer/thickness, using high current density, on metallic opals made of silica or polystyrene, followed by a selective removal of the opal [101].

The research projects focusing on the development of the techniques for using hydrogen energy is one of the most important energy–related areas. Metals with nanoporous structures have shown improved reaction kinetics and lower uptake and release temperatures. Thus, these metals could present useful properties for rapid hydrogen uptake and release. According to Tappan et al [102], the palladium – hydrogen system, has attracted more and more attention, mainly because of the easy procedure and friendly condition to produce a pure sample of palladium and these samples do not require more special surface treatments.

#### Li-ions Batteries Applications (LIBs)

Due to the increased demands for the high energy density of portable electronic devices and electric vehicles, Lithium-ion batteries (LIBs) have been intensively, investigated. It should be emphasized that batteries which obtain high energy density by storing charge in the bulk of a material can also achieve high discharge rates by using Lithium iron phosphate in nanoscale, known as LiFePO<sub>4</sub> [102-103].

Based on a research work of Kang et al [104], Ni and Cu NMFs were used to make a lithium–ion battery that can be 90% charged in two minutes. It could lead to few minutes' charge for laptop and 30 seconds' charge for cell phones. This type of cathodes, can be applied to hold as much energy as a conventional one, but can be recharged a hundred times faster [104].

According to Cheng et al [106], electrodeposited zinc foams were characterized by formation of nanoparticles on secondary dendrites in a three-dimensional network with a particle size in the range of 54.1 - 96.0 nm. The obtained nanoporous zinc anodes were also characterized by; i) highly oriented crystals, ii) high surface area and iii) more rapid kinetics in contrast to conventional zinc in alkaline media. The prepared anode material had a utilization of ~88% at full depth-of-discharge at various rates indicating a super rate-capability. The rechargeability of  $Zn^0/Zn^{2+}$  showed remarkable capacity retention over 100 cycles at a 40% depth-of-discharge to ensure that the dendritic core structure was imperforated. Upon charge-discharge cycling, the dendritic structure was densified and presented excellent performance compared to conventional zinc electrodes [105].

Tappan et al [103] have prepared three types of Sn-Cu alloys with different Sn content, different porosity and different pore size. Both capacity and cycling performance of the produced anodes, were improved by optimizing the nanostructure of the materials using electrochemical dealloying [107-108].

In addition, Cu and Sn-based NMFs electrodes have been successfully prepared using electrodeposition process. Three–dimensional porous  $Cu_6Sn_5$  alloy negative electrodes for rechargeable lithium batteries were synthesized (Figure 4.9). They were characterized by with fast mass transport and rapid surface reactions [108-110].



#### FIGURE 4.9

SEM of electrodeposited nanoporous Cu-Sn alloy electrodes. a) Large pores formed due to evolution of  $H_2$ . b) Morphology of the walls. c) Detailed porous structure of the walls [108]

The low specific capacity of the conventional graphite based anodes is one of the disadvantages that limit the capacity of lithium –ions batteries (LIBs). As stated by Guo et al [111], transition metal oxides, such as NiO, MnO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>- based anodes can be used to improve the specific capacities of LIBs for several times. However, the poor electrical conductivity of these oxides significantly limits the lithium ion storage and charge/discharge rate. The storage performance of such oxides can be developed by applying dealloying process and the formation of oxide/porous metal foams composites. These hybrid electrodes are characterized by; highly reversible specific capacity, high-rate capability and long cyclic stability [111].

According to Wada et al. [112], freestanding bulk three-dimensional nanoporous Si, were prepared by dealloying of  $Mg_2Si$  in metallic Bi melt. The produced lithium-ion batteries using such electrodes were characterized by; high capacity nearing their theoretical limits, greatly extended cycle lifetime, and considerably improved battery performance compared with electrodes made from bulk silicon nanoparticles.

#### **Fuel Cell Applications**

Porous platinum is an excellent catalyst for the electro-oxidation of fuels such as hydrogen, methanol, ethanol, formic acid or glucose as well as the electro-reduction of oxygen in fuel cells. It has the highest catalytic activities of all pure metals for the corresponding reactions. A big drawback of platinum is its high price and its limited resources as well. Therefore, the main goal in fuel cell research is to reduce the mass of platinum per surface area during fabrication by controlling the size and shape of the deposited structures. Decreasing diameters enables an increasing surface to volume ratio and thus increasing numbers of catalytically active sites per mass, which means higher platinum utilization. Moreover, controlling the microscopic shape is very critical, since different crystallographic planes of platinum show different catalytic activities. Using nanoporous metal electrodes for fuel cell catalysis may remove stability issues associated with carbon supports, and opens approaches for new catalyst design. The high surface area of porous platinum enables a high fuel turnover rate at low electrode polarization and hence a high power output of the fuel cell [113]. Another strategy is to replace a fraction of platinum by cheaper elements. In many fuel cells, the application of alloy catalysts such as Ru, Ir, or Sn to form binary or even ternary alloys, are desired, due to better resistance towards CO poisoning at the anode and an

improved tolerance towards methanol crossover effects at the cathode compared to pure platinum [114].

The objective of the work presented by Dzhafarovet al [115] was to study the performance of direct ammonia fuel cells (DAFC) using nanoporous silicon (PS) as proton conducting membrane (instead of traditional polymer Nafi on membrane) and  $TiO_2$ ,  $Au/TiO_2$  or Au as catalyst layer. Porous silicon layers have been prepared by electrochemical modification of silicon substrates. The work demonstrates that the PS based fuel cells have potential for portable applications.

#### Supercapacitors

Supercapacitors, are considered the most promising candidate as energy storage devices due to high power density, long cycling life as well as short charge/discharge time. These advantages make supercapacitors promising for use in many applications such as automotive industry, space and aeronautical industry or mobile devices [116-118]. The development of new electrodes is one of the most important areas towards the development of advanced supercapacitors. In this field, transition metal oxides are very attractive materials due to their pseudocapacitive electrochemical behavior [114].

According to G. A. Lange et al [119], in case of application as supercapacitors electrodes, properly selected metal oxides with high porosities as well as wide pore distribution, are deposited. Nanostructured metallic Cu-Fe foams were electrodeposited and examined as electrodes for supercapacitors. The morphological characterization of the deposited Cu-Fe 3-D foams were changed by increasing time of deposition as well as applied current. Due to high cathodic current, simultaneous deposition of Cu and Fe occurs with intense hydrogen evolution and thus characteristic craters, are created [119].

According to Pan et al [120], the combination of an active electrode material with a suitable

electrolyte may facilitate the development of energy storage systems with high performance and high energy density. Mesoporous  $Mn_{1.5}Co_{1.5}O_4$  /Ni foam composite electrodes were fabricated via the electrodeposition method. Further, an asymmetric supercapacitor having (MCO/Ni) positive electrode obtained after electrode psoition for 15 min, a plasma-treated activated carbon (PAC)/Ni electrode as a negative electrode, and carboxymethyl cellulose-lithium nitrate (LiNO<sub>3</sub>) gel electrolyte (denoted as (PAC/Ni)//(MCO/Ni)-15 min) was constructed. The good supercapacitive performance and excellent stability of the above mentioned device is due to the hierarchical structure and high surface area of the (MCO/Ni)-15 min electrode, which facilitates lithium ion intercalation and deintercalation at the electrode/electrolyte interface and limits volume change during long-term charge/discharge cycles [120].

# Conclusion

In conclusion, nanoporous metals (NPM) are synthesized using different techniques such as dealloying, scarifacial templating, dynamic Hydrogen bubble templating, combustion synthesis, solgel, nanosmelting. NPM are characterized by high surface area, tunable pore sizes, and high surface to volume ratio and can be functionalized.NPM are an important material that has applications in many areas such biomedical, catalysis and green energy. Nanoporous metals have been used for creating drugs for cancer, catalysis of reactions due to its high surface area, capturing hydrogen and carbon into its pores and surface, platforms for cell culture and other numerous applications. In addition, NPM could find potential applications in fields, such as sensors, actuators, fuel cells,

Lithium-ions batteries, metal-air batteries, supercapacitors, synthesis of chemicals, water electrolysis, hydrogen storage and automobile exhaust treatment.

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