Morphological Tuning of Nanoporous Metals Prepared with Conversion Reaction Synthesis via Thermal Annealing

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Supporting Information

ABSTRACT: Conversion reaction synthesis, namely, reacting an organolithium reducing agent with a metal chloride to produce a metal/LiCl nanocomposite and then removing lithium chloride with a polar organic solvent, is an efficient and scalable way to fabricate a variety of three-dimensional, bicontinuous nanoporous transition metals. Thermal annealing was investigated as a means to tune the morphology of these nanoporous metals. X-ray diffraction studies were used to investigate the effect of thermal annealing on the size and strain of phases in Cu/LiCl, Co/LiCl, and Fe/LiCl nanocomposites, while electron microscopy and nitrogen adsorption studies were used to study the porosity and surface properties of the resulting nanoporous metals after LiCl was removed from the annealed nanocomposites. Annealing metal/LiCl nanocomposites resulted in the controlled growth of the metal nanoparticles, the rate of which depended on the diffusivity of the metal. It was observed that annealing nanocomposites produced more robust nanoporous metals with increased porosity under certain conditions. Overall, it



was found that annealing the as-formed nanocomposites rather than the isolated nanoporous metals provides finer control of the conversion synthesis process and allows for the design of more optimized pore structures and thus enhanced suitability for catalytic and electrochemical applications.

1. INTRODUCTION

Nanoporous metals (NPMs) are bicontinuous interconnected networks of metal ligaments that form pores ranging in sizes from 1 to 100 nm in diameter. These pure metal structures have a low density and high surface area, giving them enhanced catalytic activity and making them promising materials for capacitor and battery electrodes.^{1–4} They also retain many of the desirable and advantageous properties of metals, such as high thermal and electrical conductivity while gaining nanostructured enhancements such as superior optical and plasmonic properties.⁵⁻⁷ The most widely researched fabrication pathway to NPMs is the dealloying method, which involves chemically or electrochemically dissolving a less-noble element from a metal alloy, with the undissolved element reforming into an NPM.⁸⁻¹⁰ The best-known example of this method is synthesizing nanoporous gold by etching silver from a silver-gold alloy.

We recently reported an alternative scalable, room-temperature synthesis route to nanoporous metals that we shall refer to as conversion reaction synthesis (CRS).¹¹ This method utilizes an organolithium reducing agent (typically *n*butyllithium) to convert metal halide precursors into metal/ lithium halide nanocomposites that are then purified with a nonaqueous polar solvent to remove the lithium halide phase and yield pure NPMs. CRS is a versatile method that can produce many varieties of NPM due to the high number of potentially compatible precursor compounds. As of this report, only metal chloride and metal bromide compounds have been used to make NPMs with CRS, but theoretically, any ionic metal compound that can be reduced by *n*-BuLi to produce an easily dissolvable conjugate Li-based compound as a reaction product is potentially compatible.

The final nanoporous morphology is highly dependent on the target metal. In the conversion step, the reaction follows the equation $MX_n + nLi \rightarrow M + nLiX$, where *n*-BuLi reduces the metal-halide precursor (MX_n) to form a solid-state nanocomposite with the resulting lithium halide compound (LiX) and pure metal (M).¹¹ Within the nanocomposites, the metal already exists as metal nanoparticles that are interconnected to form a metal ligament network. As the precursor is converted, the newly formed metal and lithium halide phases separate, and metal atoms that were previously evenly dispersed in the solution then diffuse at the reaction interface and coalesce into the metal ligament network. This mechanism is similar to the continuum model for NPMs via

Received: May 3, 2019 **Published:** July 2, 2019



Figure 1. Schematic of conversion reaction synthesis (CRS) illustrating the typical effects of purification (through washing to dissolve the lithium halide component) and the annealing of metal/lithium halide nanocomposites prior to purification as a strategy to avoid the collapse of the nanoporous framework.

dealloying by Erlebacher et al., which explains that the formation of nanoporous gold during the dealloying of a silver-gold alloy is due to continuous diffusion of gold atoms into "two-dimensional islands" at the solid-electrolyte interface during dissolution that propagate and ultimately form a porous structure.¹² In CRS, the resulting thickness of each ligament that comprises the filament structure strongly depends on the target metal's atomic mobility. Atomic mobility, in this case, refers to a metal's ability to diffuse through solids and along solid-solid interfaces and generally follows the same periodic trends as the diffusion rates of metals in an external host, where previous measurement and modeling efforts shown generally increases with atomic number.¹³⁻¹⁷ For example, a review on the diffusion of transition metals in silicon supports this claim, reporting the diffusion coefficients of Fe, Co, and Cu in silicon to be $\sim 4 \times 10^{-6}$, 1×10^{-5} , and 1×10^{-5} 10^{-4} cm²·s⁻¹, respectively.¹⁵ Metal atoms with higher mobility migrate further during the conversion reaction and collect over a longer characteristic distance, forming networks with thicker ligaments than metals with lower atomic mobility due to the thermodynamic favorability of forming structures with lower surface areas. For example, copper is more mobile than iron, so nanoporous copper (Cu NPM) consists of thicker metal ligaments and larger pores than nanoporous iron (Fe NPM), which is a less mobile metal.

The nanoporous metal network undergoes additional changes when the metal/lithium halide nanocomposites are purified by dissolution of the lithium halide.¹¹ During the conversion reaction, separate metal and halide phases are produced simultaneously in close proximity. The lithium halide phase is always more volumetrically abundant and presents an additional physical barrier that hinders the metal atoms from migrating and coalescing into larger ligaments. Consequently, using precursors that produce nanocomposites with more

lithium halide further increases these barriers and results in finer NPM structures. For example, nanoporous iron produced from FeCl₃ has a higher surface area and smaller ligament thickness than nanoporous iron from a FeCl₂ precursor (160 m²·g⁻¹ and 8 nm ligament thickness compared to 130 m²·g⁻¹ and 10 nm ligament thickness) because 50% more LiCl is produced.¹¹

The physical barriers imposed by the lithium halide are removed with its dissolution during purification, allowing the metal to reconstruct itself to minimize surface energy. The magnitude of changes that occur in response to dissolution depends on the mobility of the metal. Higher-mobility metals such as Cu exhibit extensive recrystallization and growth of the nanocrystalline domains, resulting in thicker metal ligaments. Lower-mobility metals also undergo recrystallization but typically to a much lesser degree. Metals that have a small ligament size after dissolution tend to experience structural collapse. Smaller ligament sizes are typically accompanied by decreasing interconnectivity between ligaments. Thus, when the lithium halide support is removed, it is experimentally observed that the ligament network partially collapses, resulting in an overall denser material with smaller pore widths and lower pore volumes. Figure 1 shows a schematic for these reconstruction mechanisms.

The basic CRS procedure produces only one specific NPM morphology per precursor. Therefore, it is necessary to develop procedures to gain morphological control over NPM materials so that they can be optimized for practical applications. For example, to maximize catalytic activity, nanoporous catalyst systems should have an intermediate pore size that is small enough to provide abundant exposed catalytically active sites and yet is large enough to allow a high flux of reactant atoms to those sites.^{17,18} Morphological control



Figure 2. X-ray diffraction patterns of annealed metal/LiCl nanocomposites and their corresponding purified nanoporous metals. (A) Annealed Cu/LiCl nanocomposites, (B) annealed Co/LiCl nanocomposites, (C) annealed Fe/LiCl nanocomposites, (D) nanoporous Cu from the corresponding annealed nanocomposite, (E) nanoporous Co from the corresponding annealed nanocomposite, and (F) nanoporous Fe from the corresponding annealed nanocomposite.

can also be used to mitigate the structural collapse that occurs in less mobile NPM systems, such as that of nanoporous Fe.

In this work, the effect of thermal annealing at various temperatures on Cu/LiCl, Co/LiCl, and Fe/LiCl nanocomposites was investigated as a means to control the final nanoporous morphology once the postannealed nanocomposites are purified to Cu, Co, and Fe NPMs, respectively. It was hypothesized that annealing the nanocomposite phase before purification will allow the metal nanocrystals to grow without compromising the porous structure, resulting in a thicker and more robust ligament network that will be resistant against structural collapse. Our morphological evolution of the annealed nanocomposites and the resulting NPMs provides insight into the precise nature of the interaction between the metal and lithium halide phases within the nanocomposite phase and how these interactions influence the final nanoporous structure.

2. EXPERIMENTAL METHODS

2.1. Preparation of Annealed Nanocomposites and Corresponding Purified Nanoporous Metals. Due to the air- and moisture-sensitive nature of many reaction species, all synthesis procedures are carried out in an argon glovebox (≤ 10 ppm O₂; <1 ppm H₂O). Anhydrous CuCl₂, CoCl₂, and FeCl₂ (all \geq 99.9% trace metals basis, Sigma-Aldrich) are used as precursors to produce Cu, Co, and Fe NPMs, respectively. Each precursor is first added to hexane (HPLC, Fisher Scientific) that has been desiccated with molecular sieves (Type 3A, Sigma Aldrich) for at least 48 h. Ten milliliters of hexane is used per gram of precursor. *n*-Butyllithium (1.6 M) in hexane (Sigma-Aldrich) is then added at 1.25× stoichio-

metric ratio to ensure a complete reaction. The solution is allowed to react for 24 h, and then the solids are filtered and repeatedly rinsed with fresh hexane to remove excess *n*butyllithium. The resulting powder is dried in the glovebox, resulting in a metal/LiCl nanocomposite.

In a glovebox, each to-be-annealed nanocomposite sample is sealed under vacuum in a borosilicate glass ampule with a 19.5 mm diameter and 0.8 mm wall thickness (Sigma-Aldrich), which allows for safe inert annealing. The samples were then annealed in a box furnace that was preheated to the target temperature. After 1 h of annealing, the samples are immediately removed from the furnace and cooled to room temperature before being transferred back into the glovebox so that the ampules can be unsealed without air contamination. Inside the glovebox, a small portion of each sample is removed for X-ray diffraction (XRD) characterization.

To purify the annealed nanocomposites, the sample is placed into a fritted glass filter funnel. Then, anhydrous methanol (HPLC, Fisher Scientific) is poured into the filter funnel and allowed to slowly drain out of the bottom into a collection flask. Like the hexane, the methanol is also desiccated with molecular sieves (Type 3A, Sigma Aldrich) for at least 48 h. This process is repeated a total of three times to ensure complete LiCl dissolution. The purified NPM sample is then dried in the argon glovebox.

2.2. Materials Characterization. X-ray diffraction (XRD) patterns of the nanocomposite and NPM samples were collected using a powder diffractometer (Bruker D2 Phaser) using Cu K α radiation ($\lambda = 1.5418$ Å, 40 kV, 40 mA) in a 2 θ range from 10° to 80° with a scan rate of 0.01°/s. In a glovebox, powder samples were loaded into circular sample holders and sealed with Kapton tape to prevent air

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contamination. SEM images were acquired with a Zeiss Sigma 500 scanning electron microscope.

Analysis of XRD patterns began with phase identification via search and match software (Jade, version 9) in conjunction with the International Center for Diffraction Data (ICDD) database. To determine microstructural details about these phases, Rietveld refinements were carried out in TOPAS V6 using a fundamental parameter model of the instrument profile, incorporating a 0.6 mm divergence slit, 20 mm sample length, 250 mm beam path length, and 2.5° Soller slits. For all analyses, sample displacement was refined. Due to the limited number of peaks (typically 2 or 3), the ability to distinguish between size and strain broadening is severely limited, so phase refinements were carried out including only the dominant broadening effect (Lorentzian size broadening for metals, Gaussian strain broadening for LiCl). As a result, the parameters reported here represent a lower limit for the true crystallite size and an upper limit for the true sample strain. Fit quality was assessed by both graphical analysis of the agreement between the experimental and calculated patterns and weighted profile R-factors (R_{wp}) . Further details of the refinements, examples of the fits, and discussions of the calculated parameters are provided in the Supporting Information.

 $\rm N_2$ adsorption–desorption analysis was measured with a Quantachrome Nova 4200e surface area and porosity analyzer. Each sample was loaded into a measurement cell in a glovebox and then closed with Parafilm to protect it from oxygen as it is transferred to the analyzer. Once inserted into the analyzer, each sample was degassed under vacuum at 60 °C for 12 h. $\rm N_2$ adsorption–desorption isotherms were collected at 78 K (liquid nitrogen temperature). The isotherm was then analyzed with the native Nova Gas Sorption Analyzer software to calculate the specific surface area and cumulative pore volume of each sample.

3. RESULTS AND DISCUSSION

To study the effect of thermal annealing on the structure of the nanocomposites and their corresponding NPMs, it is important to study target metals with a range of mobilities, motivating the choice of Cu, Fe, and Co for this study. From our previous investigation, it was expected that Cu has high mobility, Fe has low mobility, and Co has intermediate mobility between those of Cu and Fe.¹¹ Figure 2 shows X-ray diffraction patterns of each annealed nanocomposite (upper plot) and its corresponding NPM (lower plot). Nanocomposites were annealed at temperatures ranging from 80 °C up to 500 °C. This temperature range was large enough such that all metal groups showed significant crystallite growth while remaining safely below the melting point of LiCl (605 °C). In each case, annealing causes the XRD peaks of both the metal and LiCl phases to sharpen. The sharpening increases with temperature for all samples, with readily visible sharpening exhibited even at 80 °C by Cu. X-ray peak sharpening for these metals is primarily due to increases in the average crystallite size, a quantity that can be calculated using Rietveld refinement methods.¹⁹ This method was applied to each XRD pattern to determine the volume-weighted average metal crystallite size, with the results plotted in Figure 3.

While each distinct metal/LiCl nanocomposite responds differently to annealing, the general trend for all samples is similar with a slow growth until a characteristic temperature was reached, beyond which rapid growth occurs. At 10 nm in



Figure 3. Average metal crystallite size trends in annealed nanocomposite samples. The volume-weighted average crystallite sizes were determined by Rietveld refinement against the X-ray diffraction data shown in Figure 2. Individual plots of Rietveld refinement results and related information are given in Figure S2.

diameter, the Cu crystallites within the Cu/LiCl nanocomposites have the highest unannealed crystallite size, which then exhibits consistent growth that increases monotonically with increasing temperature. The Co crystallites within the Co/LiCl nanocomposite have a very small unannealed size, with an estimated diameter of 1.9 nm, while Fe in the Fe/LiCl nanocomposites has an exceptionally small crystallite size estimated at 0.7 nm. Compared to the Cu/LiCl nanocomposites, Co and Fe in the Co/LiCl and Fe/LiCl nanocomposites exhibit very little crystallite growth until higher temperatures were reached, remaining below 6 nm in size at a temperature up to at least 300 °C. In contrast, annealing at 300 °C causes Cu in the Cu/LiCl nanocomposite to grow to nearly 50 nm in diameter, while the same temperature only causes the metal phases of the Co/LiCl and Fe/LiCl nanocomposites to grow to 5.7 and 3.5 nm, respectively. When Co/LiCl and Fe/LiCl are annealed at 400 and 500 °C, respectively, the estimated average metal crystallite size rapidly increases to \sim 30 nm for Co and \sim 40 nm for Fe for reasons that are not yet well understood.

This type of metal coarsening has been previously studied in nanoporous metals synthesized with dealloying methods. Regardless of the synthesis method, all nanoporous pure metals should theoretically exhibit similar coarsening behavior because they are all fundamentally built from a network of interconnected metal nanocrystallites. However, it is not clear if coarsening of the metal phase within the metal/lithium halide nanocomposite will follow a similar behavior due to the presence of the halide phase, which can potentially either slow coarsening by serving as a physical barrier or serve to enhance the mobility of diffusing ions by providing a lower barrier pathway for the metal ions to diffuse. Monte Carlo simulations of nanoporous gold coarsening²⁰ suggest that porous metal coarsening is primarily a surface diffusion-controlled phenomenon that follows an Arrhenius relationship between growth rate, annealing temperature, and annealing time, a result that was corroborated by experimental X-ray nanotomography studies.²¹ Further studies^{22,23} investigated this relationship specifically in the context of metal crystallite growth within annealed nanoporous metals. The coarsening rates of the metal



Figure 4. Linearized Arrhenius plots of metal crystallite sizes within the annealed nanocomposites and corresponding estimated annealing activation energies for the metal phases. The estimation is based on the linearized form of the Arrhenius model given in eq 1. The slope of the best fit line was used to calculate the annealing activation energy required for metal crystallite growth within the different metal/LiCl nanocomposites. (A) Cu from annealed Cu/LiCl nanocomposites, (B) Co from annealed Co/LiCl nanocomposites, and (C) Fe from annealed Fe/LiCl nanocomposites.



Figure 5. SEM images of nanoporous Cu samples from purified Cu/LiCl nanocomposites annealed for 1 h at (A) room temperature (no annealing), (B) 80 °C, (C) 150 °C, (D) 200 °C, (E) 250 °C, and (F) 300 °C. BET-specific surface area is calculated from each sample's N_2 adsorption–desorption isotherm, which is given in Figure S1. All images are the same scale with 200 nm scale bars marked.

nanocrystals within the nanocomposites could be described by the following equation:^{20,21,24}

$$[d(t)]^{n} = k_{o}t \, \exp\!\left(\frac{-E}{RT}\right) \tag{1}$$

where d(t) is the crystallite diameter at time t, E is the activation energy required for coarsening, T is the annealing temperature, R is the gas constant, k_0 is a constant, and n is the coarsening exponent, which was estimated to be equal to 4. This choice of the coarsening exponent is known to be appropriate for systems with surface diffusion-controlled coarsening mechanisms and has been used previously to measure the kinetics of nanoparticle and nanopore coarsening.^{20,21,25} In a nanocomposite, surface diffusion is effectively diffusion at the metal/LiCl interface.

Figure 4 shows the calculation for the coarsening activation energy *E* for all three nanocomposite systems based on the slope of the linearized relationship between $\ln[d(t)^n/t]$ and $(RT)^{-1}$. In this calculation, values for d(t) are based on the metal crystallite sizes within the metal/LiCl nanocomposites calculated with Rietveld refinement of the X-ray diffraction patterns in Figure 2. Each sample was annealed for 1 h, so t is kept as a constant that is equal to 3600 s. The calculated activation energies for the Cu/LiCl, Co/LiCl, and Fe/LiCl systems under this assumed coarsening mechanism are 0.17, 0.28, and 0.37 eV, respectively. These extracted energies are generally consistent with the observed coarsening rates (Cu \gg Co > Fe). These values are also close to previously reported activation energies for surface diffusion of transition metal adatoms measured with ion beam microtexturing by Rossnagel and Robinson,²⁶ which is consistent with the choice of the coarsening exponent and reinforces the notion that coarsening of the metal phases is dominated by surface diffusion.^{26–28}

The morphology of the purified NPMs from the annealed nanocomposites was further analyzed with scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) analysis. Both analyses provide important insights into how the metal nanocrystal growth induced by thermal annealing affects the overall nanoporous structure. SEM images of the purified NPMs from the annealed nanocomposites are



Figure 6. SEM images of nanoporous Co samples from purified Co/LiCl nanocomposites annealed for 1 h at (A) room temperature (no annealing), (B) 100 °C, (C) 150 °C, (D) 200 °C, (E) 300 °C, and (F) 400 °C. BET-specific surface area is calculated from each sample's N_2 adsorption–desorption isotherm, which is given in Figure S1. All images are the same scale with 200 nm scale bars marked.



Figure 7. SEM images of nanoporous Fe samples from purified Fe/LiCl nanocomposites annealed for 1 h at (A) room temperature (no annealing), (B) 200 °C, (C) 300 °C, (D) 400 °C, and (E) 500 °C. BET-specific surface area is calculated from each sample's N_2 adsorption–desorption isotherm, which is given in Figure S1. All images are the same scale with 200 nm scale bars marked.

displayed in Figures 5–7 along with the corresponding BET-specific surface area inlayed in each image. The BET-specific surface area was determined from each sample's N_2 adsorption–desorption isotherm, which is available in Figure S1. Data trends on surface properties related to the annealing temperature and crystallite size are compiled in Figures 8 and 9.

The Cu NPM network behavior closely reflects the crystallite size trends in Figure 3. The consistent growth of the metal nanoparticles when annealed results in thicker metal ligaments, as shown in Figure 5A–F, and a correspondingly consistent decrease in specific surface area (Figure 8A).

Interestingly, Figure 5F shows that, once the Cu crystallites grow to a large enough size (above \sim 200 nm in diameter), they lose their interconnectivity and the porous network is destroyed. Because of this, Cu/LiCl samples were not annealed above 300 °C. The Co and Fe NPM network behaviors are more complex.

For both samples, annealing at lower temperatures (100 $^{\circ}$ C for Co and 200 $^{\circ}$ C for Fe) led to an initial sharp drop in specific surface area (Figure 6 for Co and Figure 7 for Fe). The structures then stabilize, and the surface area decreases much more slowly for samples annealed at moderate temperatures (100 to 300 $^{\circ}$ C for Co and 200 to 400 $^{\circ}$ C for Fe). However,



Figure 8. BET-specific surface areas of nanoporous metals obtained from purified annealed nanocomposite samples. Measurements are based on N_2 adsorption–desorption isotherms available in Figure S1. (A) Cu NPM from annealed Cu/LiCl, (B) Co NPM from annealed Co/LiCl, and (C) Fe NPM from annealed Fe/LiCl.



Figure 9. BET surface area and pore volume data of nanoporous metals from annealed nanocomposites, including the relations between (A) BETspecific surface area and nanocomposite annealing temperature, (B) BET-specific surface area and NPM crystallite size, (C) BET cumulative pore volume and nanocomposite annealing temperature, and (D) BET cumulative pore volume and NPM crystallite size. Specific surface area and cumulative pore volume were calculated from the N₂ adsorption–desorption isotherm of each sample, which is available in Figure S1. Crystallite sizes were obtained by Rietveld refinement against X-ray diffraction data (Figure S2).

above-threshold annealing at higher temperatures (400 $^{\circ}$ C for Co and 500 $^{\circ}$ C for Fe) causes the nanoporous structures to rapidly decrease in surface area, in each case, dropping to less than 10% of the original value. This change is apparent in Figures 6F and 7E, where the Co and Fe ligaments are

suddenly much larger than the previous images of lowertemperature-annealed samples, and their surface area decreases to less than 10 m²·g⁻¹. Both the Co and Fe NPM ligaments grow to over 200 nm in width when annealed at 400 and 500 °C, respectively. The Fe NPM ligaments grow from an average



Figure 10. Macroporosity of nanoporous metals from annealed nanocomposites estimated from SEM images (Figure S4). (A) Cu NPM from annealed Cu/LiCl, (B) Co NPM from annealed Co/LiCl, and (C) Fe NPM from Fe/LiCl. The low porosity of Fe NPMs observed at temperatures of 400 $^{\circ}$ C and below is indicative of framework collapse after LiCl removal.

width of less than 10 nm in Figure 7D to widths in excess of 200 nm in Figure 7E, while the Co NPM ligaments grow from an average width of 50 nm in Figure 6E to over 200 nm in Figure 6F.

The surface area behavior for the Co and Fe samples is a result of metal crystallite growth and the unique interactions between the metal and LiCl phases. Basic geometry states that the ratio between an object's surface area and volume follows an inverse relationship (e.g., the ratio of surface area to volume of a sphere is given by S/V = 3/R). The relationship between a nanoporous metal's specific surface area and the size of its constituent metal nanocrystals shows a similar relationship in Figure 9B, where the specific surface area of a sample increases sharply as the crystallite size approaches zero. Because the unannealed Co and Fe samples had particularly small average crystallite sizes, the small crystallite growth caused by nanocomposite annealing at a low temperature is enough to cause a sharp initial loss of specific surface area. The cobalt nanocrystals continue to grow when Co/LiCl nanocomposites are annealed between 100 and 300 °C, but because of this inverse power relationship, there is a correspondingly smaller drop in the specific surface area for the resulting Co NPMs. Fe NPM samples from nanocomposite samples annealed between 200 and 400 °C did exhibit increased temperature stability compared to the Cu and Co samples as there was very little further crystallite growth and no corresponding decrease in surface area. Figure 9C,D shows that the cumulative pore volume decreases for the three metal systems as annealing temperature increases. In fact, all three NPMs converge on the same trendline for the cumulative pore volume after being annealed at mild temperatures, regardless of the initial value. Cu and Co NPMs both have a higher initial pore volume, but after annealing at or above 100 °C, the pore volume for both systems decreases to match that of the Fe NPM. No single property explicitly accounts for this behavior as Figure 9D shows that cumulative pore volume behaves independently from metal crystallite size and pore size alone. Cu NPM has a consistently higher pore volume despite also having consistently higher ligament and crystallite sizes compared to Co and Fe NPMs, with the unannealed Cu NPM producing 0.4 $cc \cdot g^{-1}$ of pore volume with 10.8 nm crystallite size compared to 0.17 and 0.11 $cc \cdot g^{-1}$ for Co and Fe NPMs, which have unannealed crystallite sizes of 1.9 and 0.7 nm, respectively.

BET cumulative pore volume, as shown in Figure 9D, universally decreases for NPMs from annealed nanocomposites for two reasons. The first reason is that coarsening the metal

ligaments causes the entire material to densify. The second reason is that BET only measures the pore volume contributions from pores that are smaller than ~150 nm in diameter. Therefore, as the average pore size increases for all annealed samples,^{29,30} there are fewer pores small enough to contribute to BET-measured cumulative pore volume. This is apparent in the SEM images for Co and Fe NPM samples in Figures 6F and 7E, where nanocomposite annealing has produced an abundance of pores larger than 200 nm in diameter. This limitation means that cumulative pore volume cannot be directly equated to a sample's porosity, particularly for samples with larger pore diameters from nanocomposites annealed at higher temperatures.

By analyzing the NPM pores with further SEM studies, one can better estimate the macroporosity of each sample (we define macroporosity here as those analyzable by SEM). In this analysis, grayscale SEM images of each NPM sample are converted into black and white pixel map images, where black represents the void in the pores and white represents solid metal ligaments. The porosity of a sample is then calculated with the ratio between the black and white areas of the converted SEM image (Figure S4). Figure 10 shows the results of the porosity analysis for all NPM samples. Unannealed Cu and Co NPMs both have \sim 40% porosity, while unannealed Fe NPM has ~20% porosity. Without sintering of the nanocomposite, Fe NPM has significantly lower porosity than Cu or Co NPM because the Fe ligaments are so fine that they produce a porous network with very little structural integrity. As shown in Figure 1, removing the LiCl from the Fe/LiCl nanocomposite causes the network to collapse, resulting in a denser network with much lower porosity.

Nanocomposite annealing decreases the macroporosity of the Cu and Co NPMs. Initially, Figure 10A shows that the porosity of Cu NPM decreases linearly with increasing annealing temperature as average crystallite size slowly increases; the porosity only decreases from ~40 to ~30% when Cu/LiCl is annealed at 200 °C. However, Cu NPM samples from nanocomposites annealed at 250 and 300 °C show significantly decreased porosity values of ~20 and 15%, respectively. This large decrease in porosity is consistent with the observed structural collapse of the Cu NPM samples in Figure 5E,F. The porosity of the Co NPM samples also decreases as nanocomposite annealing temperature increases, but in this case, the relationship is approximately linear (Figure 10B), with the porosity of Co NPM only decreasing to ~30% when the corresponding Co/LiCl nanocomposite is annealed



Figure 11. Schematic illustration of differences between unannealed NPMs and NPMs synthesized with nanocomposite thermal annealing.

at 400 °C. Similar to the low-temperature Cu samples, the porosity of annealed Co NPM decreases as the average crystallite size increases. However, the Co NPM samples retain more porosity at higher temperatures because the porous Co networks never collapse. SEM images in Figure 6 show that none of the annealed Co NPM samples show decreased interconnectivity. Each image clearly shows pores, unlike the Cu NPM samples annealed above 250 °C.

The macroporosity of the annealed Fe NPM samples is a constant $\sim 20\%$ for annealing temperatures at and below 400 °C despite crystallite growth that is comparable to Co NPM (Figure 3). This is another effect of the collapse of the Fe NPM network during LiCl removal. Even though the average Fe crystallite size increases from ~ 1 to ~ 5 nm when the Fe/ LiCl nanocomposite is annealed at 400 °C, interconnectivity between the Fe nanoparticles does not improve, and the resulting collapsed networks have ~20% porosity. However, when the Fe/LiCl nanocomposite is annealed at 500 °C, the resulting Fe NPM exhibits ~40% porosity, which is double the porosity of other Fe NPM samples. As Figure 7E shows, Fe/ LiCl nanocomposite annealing at 500 °C produces Fe NPM with a much more robust structure with enough interconnectivity to resist collapse, which greatly increases macroporosity, although at the cost of a massive specific surface area loss after this high-temperature treatment.

A mechanism akin to Ostwald ripening³¹ should govern the annealing behavior of the metal/LiCl nanocomposites. Because each NPM consists of interconnected metal nanoparticles, their coalescence during thermal annealing is primarily due to surface diffusion, as described by José-Yacamán et al.³² This investigation studied the surface diffusion and coalescence of mobile metal nanoparticles and found that, when the diameter of a metal nanoparticle is sufficiently small, its high surface energy thermodynamically drives it to fuse and coalesce into other nanoparticles it contacts until it achieves a stable diameter and radius of curvature. The primary mechanism for this effect is diffusion of the unstable atoms at the surface of the particle (in this case, the interface between metal and LiCl), hence, the choice of the coarsening exponent in eq 1. The metal nanoparticles in the metal/LiCl nanocomposites form with stable diameters large enough so that, even though they are interconnected, we do not observe their coalescence into larger particles at room temperature. Increasing the

temperature restarts this mechanism, providing the nanoparticles with kinetic access to the thermodynamic driving force needed for further growth. The particle size distribution is not perfectly uniform, so when the temperature increases to the point where annealing begins, smaller particles are activated first because of their higher surface energy³³ and they are absorbed by their larger neighbors. This behavior is consistent with computational studies on the coarsening of bicontinuous structures, which show that the velocity of diffusing atoms increases in areas with high curvature.^{34,35} Because smaller particles and ligaments have higher curvature, they facilitate faster diffusion to larger particles and ligaments with lower curvature. In NPMs, this results in a coarser, more robust metal network with a larger average crystallite size, as illustrated in Figure 11.

When annealed at lower temperatures, the LiCl matrix that surrounds the metal forces it to grow anisotropically along established pathways within the nanocomposites rather than converging to an isotropic spherical shape with a lower surface free energy for the same particle volume. For this reason, LiCl plays an important mediating role in crystallite growth during annealing, allowing the ligaments to coarsen without collapsing the overall filament structure. When NPMs are annealed after purification, it was found that the network collapses, loses all appreciable porosity, and becomes a partially sintered mass of particles (Figure S3). However, at higher temperatures, LiCl also activates and begins to anneal, reducing its influence on metal crystallite growth and allowing the crystallites to coarsen further. Additionally, the growth of larger LiCl domains pushes metal ligaments together and accelerates the growth of both the metal crystallites and ligaments of the metal structure. The result of this accelerated growth is clear for Co NPM in Figure 6F and particularly for Fe NPM in Figure 7E, where SEM images show dramatically thicker and more crystalline ligaments for the high-temperature samples.

4. CONCLUSIONS

It is demonstrated that the morphology of nanoporous metals fabricated via conversion reaction synthesis (CRS) can be effectively controlled by carrying out thermal annealing of metal/lithium halide nanocomposites that are an intermediate in the CRS process. Thermal annealing of the metal/lithium halide intermediate allows coarsening of the nanoporous metal framework to be extended up to elevated temperatures of 300-500 °C, in contrast to annealing in the absence of the lithium halide, which quickly destroys the connectivity of the nanoporous framework, thus leading to the loss of the desirable nanoporous morphology. The LiCl matrix provides a mechanism for anisotropic growth that appears to be essential to preventing the ligament network from collapsing. Quantitative measurements of the nanoparticle growth rates indicate that the temperature required for annealing is inversely related to the target metal's mobility and suggest that surface diffusion processes are central to the growth mechanism. The rate of particle coarsening is observed to strongly depend on temperature with distinctly different behavior at different (and metal-specific) temperature ranges, and further detailed studies of isothermal kinetics will likely be required to gain an understanding of the origin of this behavior. While efforts to reinforce the filament network structure through annealing of metal/lithium halide nanocomposites were generally successful, an analysis of the Fe pore volume fraction indicated that this system was particularly susceptible to the collapse of the framework after lithium halide removal. Nanocomposite annealing widens the available morphology for NPMs produced by conversion reaction synthesis, facilitates the tuning and optimization of the porous microstructure, and increases the potential applicability of this emerging class for nanoporous materials for catalytic and electrochemical applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b04172.

Additional details for materials characterization and data analysis methods (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported as part of GENESIS: A Next Generation Synthesis Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under award number DE-SC0019212.

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