



# Development of thin porous metal sheet as micro-filtration membrane and inorganic membrane support

Wei Liu\*, Nathan Canfield

Pacific Northwest National Laboratory, Energy and Environment Directorate, Richland, WA 99354, USA

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## ABSTRACT

A reactive material processing method is developed in this work for fabrication of thin (25–200  $\mu\text{m}$ ) porous metal sheets of sub-micrometer pore sizes. A green sheet is first prepared by tape-casting of metal oxide-loaded slurry. Then, the green sheet is converted into a porous metallic structure through a high-temperature reduction process. Detailed preparation processes and characterization results are delineated with Ni materials as examples. The resulting 50  $\mu\text{m}$ -thick Ni sheet of about 50% porosity looks like a metal foil, which is strong enough to be self-supported and flexible to bending. The gas permeance and permeability, depending on the sheet thickness and preparation conditions, is ranged from  $5.0 \times 10^{-5}$  to  $4.0 \times 10^{-4}$   $\text{mol}/(\text{m}^2 \text{ Pa s})$  and from  $1.5 \times 10^7$  to  $8.5 \times 10^7$  Barrer, respectively. Such porous metal sheets may be used directly as a micro-filtration membrane or serve as an inorganic membrane support platform. This innovation makes it possible to develop thin flat sheet inorganic membranes with surface area packing density similar or comparable to polymeric membrane sheets.

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## 1. Introduction

Inorganic membranes provide some unique performance attributes that complement the polymeric membranes, and are attractive for a number of existing and future applications. For example, its chemical stability is much desired for filtration or separation processes that involve hydrocarbons, oils, or organic solvents. Its thermal stability provides a large window of operation temperature for adoption of membrane technologies, since many industrial process streams are hot and cooling/heating is associated with significant capital cost and energy consumption. In addition to the separation process requirements, membrane synthesis conditions are the other important consideration for a thermally stable inorganic support structure. Many high-performance membranes, such as zeolite and Pd alloy, involve a preparation step that has to be conducted at high or elevated temperatures.

A tremendous amount of progress has been made in the inorganic membrane field for recent two decades. However, its widespread application has not happened yet, compared to the large polymeric membrane industry. Its high cost per unit surface area and low surface area packing are commonly viewed as the main hindrance [1]. In sharp contrast to fruitful exploration of new membrane materials and/or new applications, research

publications on advancement of novel support materials and/or structures have been very limited. The inorganic membrane supports are an important field for technical innovation and scientific discovery.

Recently, development of ceramic monolithic membrane modules of small channel sizes ( $\sim 1$  mm) [2,3] and capillary inorganic membrane tubes [4–6] has been reported. These product concepts show promising progress toward getting the surface area packing density of inorganic membranes close to polymeric hollow fiber membranes.

In this work, we aim to develop thin porous metal sheets that allow the inorganic membranes to be fabricated with a surface area packing density equal or comparable to flat sheet polymeric membranes. For this type of membrane product design, manufacturing and engineering capabilities developed in the polymeric membrane field may be utilized to make the inorganic membrane product and module.

A variety of metals are made as foams or screen products commercially [7], which include aluminum, copper, zinc, nickel, silicon, Inconel, silver and gold. These structures typically have pore sizes from tens to hundreds of micrometers, which are too large to be an effective membrane support. In addition, the metal foam is mechanically too weak to be used as thin sheets ( $< 300$   $\mu\text{m}$ ). Traditional preparation methods of porous metallic materials include powder metallurgy process, casting, and deposition technique [8]. For example, aluminum foams are formed by casting of molten metal with blowing gas or a gas-generation agent [9–11]. The

\* Corresponding author. Tel.: +1 509 375 2524.  
E-mail address: [wei.liu@pnl.gov](mailto:wei.liu@pnl.gov) (W. Liu).

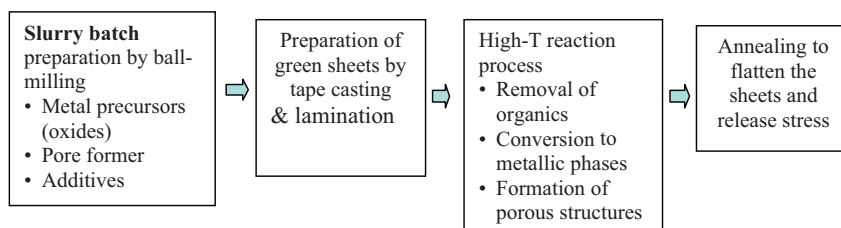


Fig. 1. Outline of a material processing route developed in this work for fabrication of thin porous metal sheets.

porous Ti, NiTi alloy, stainless steel, and Ni are made through the powder metallurgy processes [12–15], which typically use metals as a starting material and produce porous structures by controlling sintering conditions and/or using pore formers. The pore size generally correlates with the particle size of the starting metallic particles. For example, a defect-free Pd–Cu–Ni alloy membrane for hydrogen permeation was prepared on a sintered porous Ni disk support made of fine Ni powder [16]. Among sintered porous metal plates and filter products, Ti material has generated a considerable interest. Fine Ti powder may be produced from Ti hydride precursor materials [17,18] and by using a gas atomization furnace [19]. However, disks, plates or sheets made by vacuum sintering of resulting fine Ti powder still show large pore sizes, ranged from a few to tens of micrometers. A TiO<sub>2</sub> coating can be applied on to such porous Ti plates to make the surface smooth and suitable for micro-filtration application [20,21].

A quality support structure is necessary for deposition of high-performance membranes. The desirable properties of a support structure in the authors' view are (i) light, highly permeable, mechanically strong and flexible; (ii) chemically stable – resistant to solvent attack; and (iii) thermally stable – enabling membrane processing and/or separation operation at elevated temperatures. These performance attributes are contradictory to each other and are difficult to realize simultaneously with conventional fabrication methods.

In our approach, tape casting technique is combined with high-temperature reaction processes to form porous metal sheets that possess the above-listed performance characteristic. The tape casting is commonly used for preparation of polymeric membrane sheets and is also well established for the manufacturing of ceramic papers or tapes. High-temperature reactions resorted in the steel-making process provide a useful reference for the present preparation of porous metallic membrane sheets out of non-metallic starting materials, such as metal oxides and ores. The cost of metallic particles steeply increases with decreasing particle size. By contrast, metal oxides are widely available with crystalline sizes from tens of nanometer to hundreds of nanometer. In addition, the small metallic particles can become very reactive and even explosive, which imposes a serious safety concern for handling and processing. By using the metal oxide precursor, we expect that strong bonding of small metal grains is formed during reduction process of the metal oxide into metallic phases. Thus, a strong, thin porous metal sheet may be obtained.

## 2. Experimental

### 2.1. Outline of porous metal sheet fabrication process

Major process steps proposed for the preparation of porous metal sheets in this work are outlined in Fig. 1. First, a batch of slurry is prepared by mixing the metal precursor, pore former, and additives with a solvent. Then, the homogenous slurry is cast into sheets of desired dimensions by tape-casting. Two or more cast sheets

may be laminated into one green laminate. The green sheet or laminate is treated under high-temperature reaction conditions. In this process step, removal of all the pore former and organic additives, conversion of the metal precursor into the desired metallic phase, and formation of porous structures occur concomitantly. Finally, the raw porous metal sheet is annealed under suitable gas environment and conditions, and its surface is smoothed at the same time.

We expect that the present fabrication process helps decoupling of material forming processes at atomic, nano-, micro-, and macro-scales by adjusting and controlling individual process steps. For example, chemical compositions of the final metal product are determined by the slurry batch compositions, while its metallic crystal phase and pore structures can be controlled by the reaction conditions. The targeted pore size of the final product may be achieved by using the metal oxide precursor particles and/or pore formers of proper sizes, while the porosity is determined by the pore former loading and sintering conditions. The details of each process step are described in the following sections with preparation of porous Ni sheets as examples.

Pure Ni is prone to oxidation in an O<sub>2</sub>-containing gas environment around 400 °C and is also reactive in acidic solutions. However, thermal stability of the pure Ni can be significantly enhanced by modifying the Ni surface with a ceramic coating, such as nano-zirconia [22]. It is expected that the thermal and chemical stability of a porous Ni sheet can also be improved by making Ni alloys.

#### 2.1.1. Batch preparation

A batch container was filled with an appropriate amount of zirconia milling media (9 mm diameter barrel media from ER Advanced Ceramics). A solvent, such as a mixture of Methyl Ethyl Ketone (MEK) and Ethanol (80/20 volume ratio), and dispersant such as Witco Emphos PS-236 were added into the batch container and mixed. Then, the pore former was added into the container. In this work, carbon black (Cancarb Ultra Pure N990) and graphite (Asbury Graphite #4006) powder were evaluated as a pore-forming agent. Next, the NiO powder was added into the container. The resulting mixture was ball milled at a speed about 180 rpm for a minimum of 10 h. Typically, long milling time and high rolling speed would aid break-up of agglomerates of the pore former and NiO powder. Finally, the binder such as PolyVinylButyral (PVB) (Solutia Butvar B-79) and BenzylButylPhthalate (BBP) (Alfa Aeser) plasticizer were added into the container. The final mixing was conducted at a slower speed (about 110 rpm) for a minimum of 4 h. Addition of a binder tends to increase the viscosity, and therefore requires a slower rolling speed to allow the media to move through the slurry. The trapped air bubbles were removed from the slurry by rolling the slurry at a very slow speed (about 20 rpm) overnight prior to casting. Table 1 lists one representative slurry batch composition used for preparation of the green sheet with 60 vol.% carbon pore former. Specific examples for different batch compositions can be found in the patent publication [22].

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