

High Surface Area Metal Electrode

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ABSTRACT

Electrodes are one essential component in electrochemical conversion devices used for energy storage and generation. In this presentation, micro- and nano-engineered electrodes made of metallic backbones will be introduced. The electrode comprising a thin porous metal sheet of pore sizes at micrometer and sub-micrometer level, provides about an order of magnitude higher surface area density than conventional metal foams, meshes, and dense foils. Furthermore, catalytic materials such as carbon nanotubes can be grown inside the pore of the metal sheet to further increase the electron/reactant contact area. The new electrode materials have potential for applications to alkaline water electrolysis, alkaline fuel cells, battery, and ultra-capacitor.

Keywords: electrode, porous metal sheet, electrochemical reaction, high surface area, electrolysis

1 BACKGROUND

Electrochemical conversions are used in many important industrial processes and have become increasingly important for energy and environmental sustainability. Hydrogen and oxygen, which are two widely used gases, can be produced by electrolysis of water on an electrolysis cell from renewable energies, such as wind and solar power. Vice versa, electrical power can be produced by combusting hydrogen with oxygen on a fuel cell. Rechargeable batteries, which are widely used in electronic equipment and electrical cars, all involve reversible electrochemical reactions. Further more, the electrochemical reaction plays a key role in some emerging processes, such as production of ammonia from water and nitrogen with electrical power. The small-sized electrochemical ammonia production unit can be used to produce ammonia on demand, such as providing ammonia for selective catalytic reduction of nitric oxides on vehicles. The large-size unit can be used to produce ammonia from wind or solar power as fertilizer or chemical energy storage medium.

One common need for these electrochemical devices is an electrode that can provide high surface area for electrons to react with reactants per unit volume, i.e., specific surface

area. Great amounts of research and development efforts have been devoted toward discovery of new reaction chemistry, improvements of electrolyte materials, improvements of catalysts, and formulations. By contrast, the improvements to backbone structures of the electrode has been limited by availability of current material products.

A variety of metals are made as foams or mesh products commercially [1], which include aluminum, copper, zinc, nickel, silicon, Inconel, silver and gold. These structures typically have pore sizes from tens to hundreds of micrometers. In addition, the metal foam is mechanically weak to be used as thin sheets (<200 μ m). Traditional preparation methods of porous metallic materials include powder metallurgy process, casting, and deposition technique [2]. For example, aluminum foams are formed by casting of molten metal with blowing gas or a gas-generation agent [3-5]. The porous Ti, NiTi alloy, stainless steel, and Ni are made through the powder metallurgy processes [6-9], 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 [10]. 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 [11, 12] and by using a gas atomization furnace [13]. 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.

2 THIN MICRO-POROUS METAL SHEET

Recently, a new process [14] has been developed by Molecule Works Inc. (MWI) to produce thin porous metal sheets of uniform pores at sub and micro-meter scale (Figure 1). The porosity is comparable to the other porous metallic products. The micro-porous metal sheet is designed with uniform porous structures that can be controlled by the batch composition and production conditions (Figure 2). A 50 μ m-thin 20cmx20cm nickel sheet looks like a metal foil and provides a smooth surface. It is expected that nano-

catalysts, electrolyte and reactants in the electrode can be effectively confined inside such small pores to obtain a large multiphase reaction area with reduced mass transport resistance. This kind of metal sheet is recently launched by MWI as a ThinSieve™ metal sheet product.

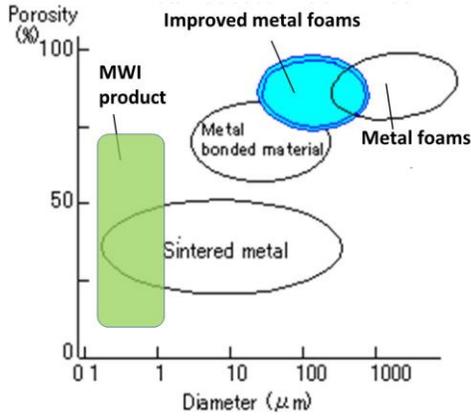


Figure 1: Micro-porous sheets developed at Molecule Works Inc. in comparison to other porous metal materials.

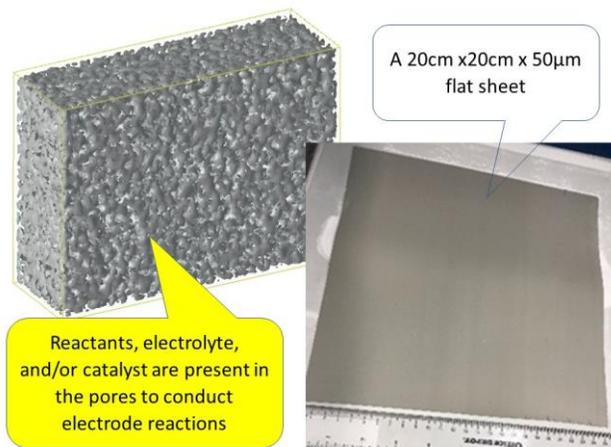


Figure 2: Uniform porous structure design and an actual ThinSieve™ metal sheet.

Impact of structural parameters of a porous metal sheet on its surface area enhancement relative to a dense metal foil is described by the following equation:

$$F = \frac{SA_r}{SA_g} = \frac{4\delta_e \cdot \varepsilon}{d_p} \quad (1)$$

Where F = enhancement factor, SA_r = electron/chemical reacting area, SA_g = geometric surface area of the sheet, δ_e = sheet thickness, ε = porosity, and d_p = pore diameter.

The enhancement factor is 1 for a dense metal foil-based electrode. With a porous metal sheet of $50\mu\text{m}$ -thickness (δ_e), 50 % porosity, and $0.5\mu\text{m}$ mean pore size (d_p), the enhancement factor is 200. It is noted that extent of the impact of porosity on the enhancement factor is limited. The difference is only by a factor 2 for a highly porous sheet (0.70) relative to low porosity one (0.35). For a constant porosity, the impact of pore size is dramatic. The enhancement factor for a sheet of $0.1\mu\text{m}$ pore can be 10 times of the $1\mu\text{m}$ -pore sheet and 100 times of the $10\mu\text{m}$ -pore sheet. Impact of the sheet thickness on the enhancement factor is also limited, because the transport resistance for the reactant to get inside the electrode and for the product to get out of the electrode would proportionally increase with the sheet thickness.

The volumetric productivity of an electrode is an important parameter for electrochemical devices and related to the volume-specific surface as described below:

$$SA_V = \frac{SA_r}{V_e} = \frac{4\delta_e}{d_p} \quad (2)$$

The specific surface area increases with decreasing pore size in inverse first order. Thus, reducing pore size in a porous electrode is a determining factor to enhancement of electrochemical reacting area.

Porosity is another important parameter for porous metal sheets. It can be measured as geometric porosity and sorption porosity as described by the following two equations:

$$\varepsilon_g = 1 - \frac{\rho_g}{\rho_m} \quad (3)$$

$$\varepsilon_l = \frac{V_l}{V_g} \quad (4)$$

Where ε_g = geometric porosity, ρ_g = geometric density, ρ_m = material density, ε_l = sorption porosity, V_l = volume of liquid sorption, V_g = geometric volume.

The geometric porosity is simply measured based on the weight and volume of a porous metal sheet relative to its material density. The liquid sorption porosity can be measured by the amount of the liquid that can be uptaken by a given volume of the porous metal sheet. The liquid fluid used in the measurement should be fully wettable. Thus, if all the pores are connected in a porous metal sheet,

the geometric porosity should be equal to the liquid sorption porosity. If the sorption porosity is less than the geometric porosity, some fraction of the pores is not accessible by the liquid. As an effective electrode structure, the porous metal sheet should have the liquid sorption porosity same or very close to the geometric porosity. For the porous metal sheet structures shown in Figure 2, the liquid sorption porosity is the same as the geometric porosity.

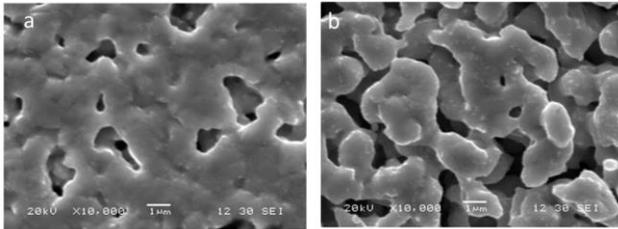


Figure 3: Surface structures of 50 μ m-thin Ni sheet with different porosity: a= 35%, b=55%.

The extent of porous networking increases with porosity as shown in Figure 3. Porosity for the present micro-porous metal sheet is preferred to be above 35% to make majority of the pores inside the sheet be connected each other. The networked porous structures are evidenced by comparing the surface to the fractured wall (Figure 4). The three sheets of different thickness all show uniform porous structures.

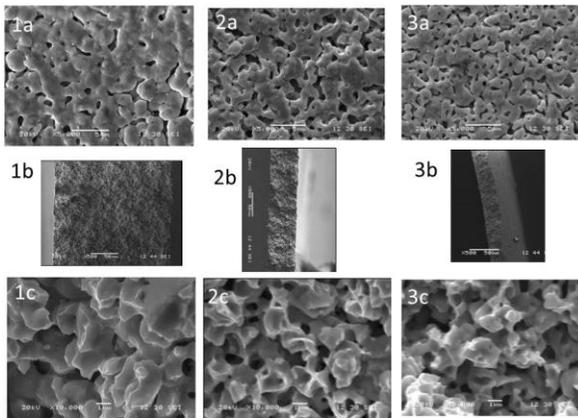


Figure 4: Porous structures of Ni sheets at different thickness: 1 = 100 μ m, 2 = 50 μ m, 3 = 25 μ m, a = surface texture, b= wall thickness, c=fractured wall.

The pore size of a porous metal sheet can be physically examined under microscopy. For the micro-porous metal sheet, the pore size is better quantified by use of established analytical procedures in the field. The external pore size of

a porous metal sheet can be characterized by mercury porosimetry technique. The capillary flow is another common method to characterize pore size distribution of a porous metal sheet. Different from mercury porosimetry, the capillary flow technique measures the pore size on the gas flow path, i.e., along the sheet thickness. Figure 5 shows the pore size distribution of the two porous metal sheets with different thickness. The pore size is within the range of 0.1 to 0.8 μ m, i.e., sub-micrometer level.

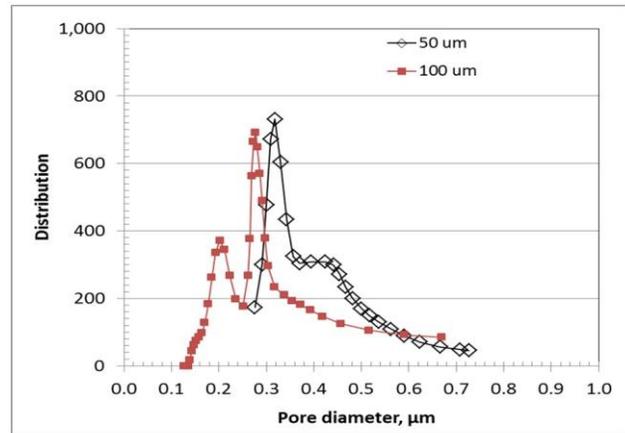


Figure 5: Pore size distribution of porous Ni sheets measured by capillary gas flow.

Nano-features can be grown inside pores of the micro-porous metal sheet by hydrothermal reaction or chemical vapor deposition. Figure 6 shows nano-catalyst particles grown inside the pores of a 50 μ m-thin porous Ni sheet. Under low magnification (Fig 6a), the support pores are intact. Under high magnification (Fig 6b), it is evident that the nano-catalyst particles or clusters are deposited on the metallic grain. Growth of carbon nanotubes inside the pores is illustrated in Figure 7. The support pores and nanotubes can be seen under low (Fig7a) and high (7b) magnification, respectively.

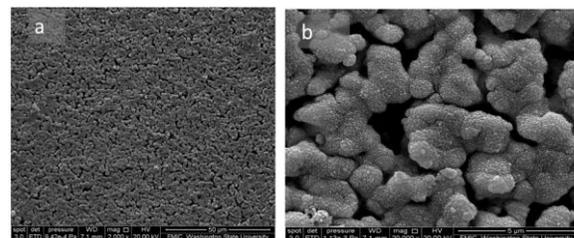


Figure 6: Growth of nano catalyts inside the pores.

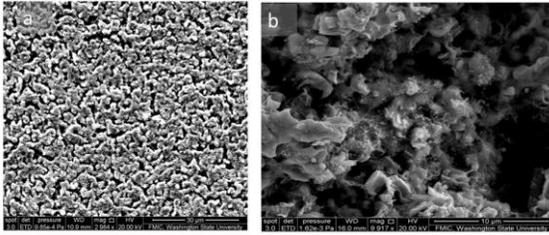


Figure 7: Growth of carbon nanotubes inside the pores

3 ELECTROCHEMICAL REACTIVITY OF MICRO-POROUS METAL SHEET

The enhancement effect of the micro-porous metal sheet electrode on electrochemical reactivity is illustrated by water electrolysis in a KOH solution in Figure 8. Under the same reaction conditions, the micro-porous Ni sheet provides a few times higher current than the dense Ni foil of the same thickness and the metal mesh of 1.0mm thickness. A few times of current enhancement was also demonstrated at different temperatures and under different voltages applied. It is projected that the degree of enhancement should be further increased by minimizing gas polarization outside the metal sheet electrode.

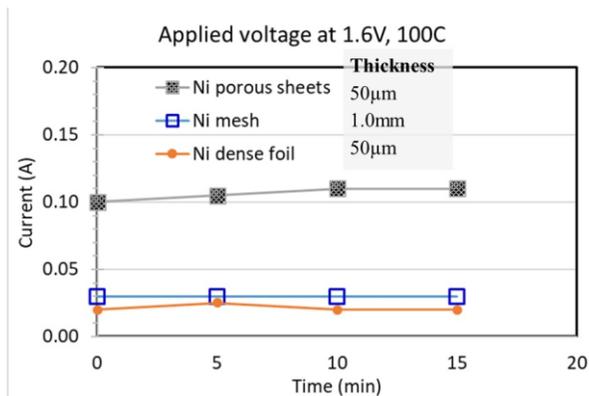


Figure 8: Water electrolysis in KOH solution with different metal sheets as the electrode.

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