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Processing, Microstructure, and Oxidation Behavior of Iron Foams

HYEJI PARK, YOONSOOK NOH, HYELIM CHOI, KICHEOL HONG, KYUNGJUNG KWON, and HEEMAN CHOE

With its historically long popularity in major structural applications, the use of iron (Fe) has also recently begun to be explored as an advanced functional material. For this purpose, it is more advantageous to use Fe as a porous structure, simply because it can provide a greater surface area and a higher reaction rate. This study uses a freeze-casting method, which consists of simple and low-cost processing steps, to produce Fe foam with a mean pore size of 10 μm. We examine the influences of various parameters (i.e., mold bottom temperature, powder content, and sintering time) on the processing of Fe foam, along with its oxidation kinetics at 823 K (550 °C) with various heat-treatment times. We confirm that Fe₂O₃ and Fe₃O₄ oxide layers are successfully formed on the surface of Fe foam. With the Fe oxide layers as an active anode material, the Fe foam can potentially be used as a three-dimensional anode current collector for an advanced lithium-ion battery.

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I. INTRODUCTION

Iron (Fe)-based materials are one of the most friendly and common materials in both our daily lives and major industrial areas, because they have been widely used as the most important structural material for items such as weapons, machine tools, vehicles, and building components over hundreds of years, owing to their low cost and superior mechanical properties.[1] Recently, use of Fe-based materials has been extended to functional materials as well, in applications such as catalysts,[2] environmental protection,[3] sensors,[4] lithium-ion batteries,[5] and biomaterials.[6,7] Furthermore, Fe-based materials are likely to become even more popular with the discovery that they can also be made porous, i.e., in the form of three-dimensional (3-D) Fe-based foam, which is expected to offer particular advantages as an advanced structural and functional material owing to its 3-D structure, low cost, low weight, large specific surface area, and high impact absorbability, along with high mechanical strength and high stiffness-to-weight ratio.[8–10]

Only during recent years, several studies have been reported on the processing and properties of Fe foam manufactured by a variety of processes, such as powder metallurgy,[6,11] gas foaming,[12] slag foaming,[13] hollow spheres,[14] and lotus-type[15,16] most likely for structural applications. Therefore, there still exists considerable demand for developing Fe foams with controlled porosity, pore size, and strut width to be potentially applied as a ‘platform’ material for various functional fields described above.

In this study, Fe foam was synthesized through a freeze-casting or ice-templating method, followed by the formation of Fe oxide on the surface. We are particularly interested in this method, because the freeze-casting method is known for producing micrometer-scale porous structures with facile, low-cost processing steps. This method consists of freezing a slurry in a mold with a cold surface, sublimating the frozen slurry under reduced pressure and low temperatures, and subsequent sintering, in order to produce a 3-D directional porous structure with uniformly distributed pores a few tens of micrometers in diameter.[17–23] This paper discusses the morphological influences of various parameters (i.e., mold bottom temperature, powder content, and sintering time) on both the processing of Fe foam and its oxidation behavior and kinetics. Finally, the implications for its potential use as an advanced energy material are briefly discussed.

II. MATERIALS AND PROCEDURES

A. Preparation of Iron Foams Using Freeze-Casting

Iron oxide (Fe₂O₃) powder (mean particle size <5 μm and purity ≥99 pct, Sigma-Aldrich, Co., USA) and a binder (polyvinyl alcohol, M₉₀ = 89,000-98,000, purity >99 pct, Sigma-Aldrich, Co., USA) were used to make a slurry. The slurry was prepared by mixing 10 ml
deionized water with 4 wt pct binder. The slurry was dispersed by a stirring and sonication process. It was then poured into a Teflon mold (28 mm inner diameter, 70 mm height) onto the top of a copper (Cu) rod, which was cooled using liquid nitrogen. The temperature of the tip of the Cu rod was controlled by heaters. To determine the effect of the powder content of the slurry, the tip temperature of the Cu rod was fixed at 263 K (−10 °C), and the powder content of multiple slurry mixtures was controlled at 10.5, 14.1, and 19.0 vol pct. Additionally, the powder content was fixed at 14.1 vol pct, while the tip temperature of the Cu rod was controlled at 263 K, 243 K, and 173 K (−10 °C, −30 °C, and −100 °C) to determine the effects of the tip temperature of the Cu rod. After freezing, the frozen slurry was freeze-dried for about 48 h at 183 K (−90 °C) and 5 × 10⁻³ torr. The green body was reduced and sintered in a tube furnace in an H₂–95 pct Ar gas mixture with a flow rate of 1.0 L min⁻¹. The reduction was performed at 573 K (300 °C) for 2 hours, and then at 773 K (500 °C) for 2 hours, and the sintering was performed at 1223 K (950 °C) for 14 hours with a heating rate of 278 K (5 °C) min⁻¹.

The microstructure of the Fe foams was observed by optical microscopy (PME 3, Olympus, Japan) and scanning electron microscopy (SEM; JSM7401F, JEOL, Japan). The pore and strut sizes were measured by optical microscopy, and porosity was measured by ImageJ Pro (Image-pro plus, Media Cybernetics, Inc.). The composition of the Fe foams was characterized using X-ray diffraction (XRD, Rigaku, D/MAX2500, Japan). The pore distribution was measured by mercury intrusion porosimetry (MIP).

B. Oxidation of Iron Foams

Fe foams were thermally treated at 823 K (550 °C) for 10, 30, 60, or 180 minutes. The microstructure and the thickness of the Fe oxide layer formed on the Fe foam were observed by SEM (JSM7401F, JEOL, Japan). The weight of the Fe oxide layer was measured by the weight difference of Fe foams before and after heat treatment. Furthermore, atomic force microscopy (AFM, XE-100, Park System Corp., Republic of Korea) was used in contact mode to examine the surface roughness of the Fe foams after the formation of the oxide layers.

III. RESULTS AND DISCUSSION

A. Microstructural Observation

Figure 1 shows SEM micrographs of a representative Fe foam processed for this study, which show a natural top surface (Figure 1(a)) and fractured surface (Figure 1(b)). With water used as a solvent, the microstructure of Fe foam generally exhibits lamellar structure due to the characteristic of ice crystal growth. Although the ice crystals tend to grow in both the parallel and perpendicular directions to the temperature gradient, they predominantly grow in the parallel direction to the temperature gradient.[17] Therefore, ice plates are formed, which are aligned along the freezing direction.

Figure 2 compares the XRD patterns of the freeze-cast foam before and after the reduction/sintering process in a tube furnace in an H₂–95 pct Ar gas atmosphere. In the reduction process, H₂O is produced as a byproduct. The reduction process consists of two different steps, both resulting in an H₂O byproduct. The first step is the reduction of Fe₂O₃ to Fe₂O₄ and the second step is the reduction of Fe₂O₄ to the metallic Fe, as described in the following reaction equations:[24]

\[3\text{Fe}_2\text{O}_3 + \text{H}_2 \rightarrow 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} \quad [1]\]

\[\text{Fe}_3\text{O}_4 + 4\text{H}_2 \rightarrow 3\text{Fe} + 4\text{H}_2\text{O}. \quad [2]\]

The H₂O byproduct formed on and in the Fe foam is expected to evaporate quickly and not affect the foam’s structure, because the reduction process was carried out at 573 K (300 °C) to 773 K (500 °C) and the Fe foam was reduced continuously at such high temperatures in an H₂–95 pct Ar gas with a flow rate of 1.0 L min⁻¹. Furthermore, according to the XRD patterns obtained, the Fe oxide powder was perfectly reduced and sintered to Fe foam. This observation on the reduction process is indeed consistent with the Fe oxide reduction process details provided by a previous study.[25]

In Figure 3, the mean pore size and porosity are shown, along with the corresponding microstructural images, for the Fe foams created by varying the mold bottom temperature from 263 K, 243 K (−10 °C, −30 °C), down to 173 K (−100 °C) with the powder content fixed at 14.1 vol pct. With the decrease in mold bottom temperature from 263 K to 173 K (−10 °C to −100 °C), the mean pore diameter decreased from 32.9 ± 7.5 to 6.9 ± 2.5 μm. This tendency can be explained by the supercooling effect on the competition between ice nucleation and crystal growth.[17,23] Supercooling is the driving force for ice nucleation and also is a critical factor that affects the size and number of ice crystals. Under a higher supercooling, i.e., the slurry being frozen at a lower temperature, the ice nucleation rate is higher than the crystal growth rate, because ice nucleation process is kinetically more favorable than crystal growth process.[26] As a result, smaller pores are formed through a lower mold bottom temperature with a higher freezing rate; in other words, the lower the mold bottom temperature, the finer the pore structure.

Additionally, the mean strut size and porosity are shown in Figure 4 for the Fe foams created by varying the powder concentration at 10.5, 14.1, and 19.0 vol pct with the mold bottom temperature fixed at 263 K (−10 °C) along with their corresponding microstructural images. With the increase in Fe oxide powder content from 10.5 to 19.0 vol pct, the strut width increased from 6.3 ± 2.2 to 25.2 ± 6.0 μm, but the porosity decreased from 77.7 ± 3.5 to 51.1 ± 8.6 pct, as expected. Apparently, with increasing Fe oxide powder content in the slurry, the strut width increases but the porosity decreases. This is somewhat expected, because with
increasing Fe oxide content, more Fe oxide particles are pushed in the interdendritic spaces forming thicker struts and, hence, thinner ice dendrites.\textsuperscript{27}

It is worth noting that uniform microstructural features were obtained for the three different powder compositions with the increasing powder content from 10.5 to 19.0 vol pct as shown in Figure 4. A lower volume fraction of powder (less than 6 vol pct) can be dispersed relatively easily, but at higher volume fractions a homogeneous suspension of powder is more difficult to achieve due to a higher ‘drag force’ between them.\textsuperscript{28} In other words, the closer the particles are packed with a higher powder concentration, the less the homogeneous suspension of powder is obtained due to stronger particle interactions. Additionally, Fe oxide powder concentration can also have a strong influence on the pore morphology.\textsuperscript{27,29,30} For example, the threshold powder concentration, above which the osmotic pressure exceeds the capillary pressure with directional pores no longer being formed, is defined as the ‘breakthrough concentration’.\textsuperscript{29} A low value of breakthrough concentration thus implies that the solid/liquid interface can engulf the oxide particles with relative ease, thus tending to result in non-directional pores at a comparatively wide range of oxide
The oxide powder composition of all samples used in this study did not appear to exceed the breakthrough concentration, resulting in directional pores in all samples as seen in Figure 4. On the other hand, the sample with the oxide powder concentration at 19.0 vol pct started to show some degree of non-directional pores (Figure 4(f)), suggesting that the breakthrough concentration for the Fe foams synthesized in this study should be a value only slightly greater than 19.0 vol pct.

To determine the average pore size distribution and the total porosity of the Fe foam, we used MIP. For this analysis, Fe foam, which was created with a solvent content of 10 ml and a powder content of 14.1 vol pct, was fabricated by setting the mold bottom surface at a temperature of 258 K (−15 °C). Figure 5 shows the pore diameter distribution curves of the Fe foams, as measured by MIP. A single sharp peak of pore size distribution lies near the pore diameter of 10 μm. Based on the MIP measurement result, the total porosity and total pore area of the Fe foams are 57 pct and 0.09 m² g⁻¹, respectively. This total pore area was used to calculate the oxidation weight gain as discussed in the following section.

B. Oxidation Behavior of Iron Foams

The successful formation of Fe₂O₃ and Fe₃O₄ oxide layers on the surface of Fe foam can provide a few important practical implications. For example, with the oxide layers as an active anode material, Fe foam could be used as an advanced anode current collector in a lithium-ion battery. If such a 3-D porous metal is used as a current collector, it is expected to improve the cyclic performance with the following several advantages. First, use of the Fe₂O₃ and Fe₃O₄ oxide layers as an active anode material produces an increase in the capacity of the anode by up to 96 pct as compared with graphite anode materials. Second, the 3-D connected Fe foam can buffer any volume expansion caused by the change of stress during charging/discharging. Third, Fe foam offers a large contact area between the active oxide material and itself and hence
offers fast pathways for electrons and ions and provides more power generation. Fourth, the active material can be formed directly on the Fe foam without any additive or polymer binder being applied, because the formation of Fe$_2$O$_3$ and Fe$_3$O$_4$ oxide layers is natural and thermodynamically favorable at high temperatures.

Therefore, we formed and examined oxide layers of Fe$_2$O$_3$ and Fe$_3$O$_4$ on the surface of the Fe foam by applying a simple thermal oxidation method. A heat treatment was carried out at 823 K (550 °C), at which temperature hematite (Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) oxides are thermodynamically more favorable in comparison to wustite (FeO) oxide according to the phase diagram$^{[34]}$ and the Ellingham diagram for Fe and O.$^{[35]}$ Since all the samples were thermally treated at 823 K (550 °C) for oxidation tests, the initial formation of wustite (FeO) oxide could be avoided. Instead, the metallic Fe first oxidizes to Fe$_3$O$_4$, which then further oxidizes to Fe$_2$O$_3$ with both the oxidation reactions showing negative Gibbs free energies (−430 kJ mol$^{-1}$ for the former and −240 kJ mol$^{-1}$ for the latter) based on the Ellingham diagram.$^{[35]}$ This thermodynamic stability observation is in good agreement with the XRD pattern results in Figure 6 where the XRD patterns of the Fe foams with heat treatments at 823 K (550 °C) for 10, 30, 60, and 180 minutes are shown; with increasing heat-treatment time, the XRD peaks of the Fe$_3$O$_4$ phase are less noticeable, whereas those of the Fe$_2$O$_3$ phase are more noticeable.

Figure 7 shows the SEM micrographs of the natural surface of an Fe foam strut after being heat-treated at 823 K (550 °C) for 30 minutes. Fe oxide layers a few hundred nanometers in thickness were formed uniformly on the surface of the Fe foam. The outside surface of the Fe foam strut was coated with a relatively smooth and continuous Fe oxide layer with an average thickness of about 0.7 μm. Surface roughness was measured quantitatively using AFM; the corresponding AFM image for the Fe oxide layer is shown in Fig. 7—SEM (a, b) and AFM (c) images of the surface of Fe foam heat-treated at 823 K (550 °C) for 30 min.

Fig. 8—Iron oxide layer thickness versus heat-holding time and (inset) SEM images of the Fe foam heat-treated at 823 K (550 °C) for 10, 30, 60, and 180 min.

![Graph](image-url)
shows the parabolic rate constant ($k_p$) evaluated for the Fe foam oxidation in this study, which is compared with other reported values obtained under similar experimental conditions. The parabolic rate constant of the oxidation of the current Fe foam is calculated to be $5.0 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ sec}^{-1}$, which is comparable to those reported in other studies: $2.7 \times 10^{-11}$ and $2.0 \times 10^{-11} \text{ g}^2 \text{ cm}^{-4} \text{ sec}^{-1}$.\(\text{[37,38]}\)

### IV. SUMMARY AND CONCLUSIONS

Fe foams with micrometer-scale pores were synthesized through a directional freeze-casting method, which is known to be industrially friendly, where an Fe$_2$O$_3$ powder aqueous slurry was directionally frozen, freeze-dried, hydrogen-reduced, and then sintered. Major processing parameters (i.e., mold bottom temperature, powder content, and sintering time) were varied to examine their effects on the processing and morphology of Fe foam. With a simple heat treatment at 823 K (550 °C), a uniform oxide layer was created on the surface of the Fe foam. Its oxidation behavior and kinetics were discussed, along with the implications for its potential use as an advanced energy material.

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