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Surface-oxidized, freeze-cast cobalt foams: Microstructure, mechanical properties and electrochemical performance

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ABSTRACT

Cobalt with anisotropic open porosity is fabricated by directional solidification of aqueous slurries of nanometric Co_3O_4 powder where ice dendrites push powders into aligned interdendritic spaces, followed by ice sublimation, reduction of the oxide to metallic Co powders, and sintering of these Co powders into parallel lamellae. As the Co_3O_4 powder slurry fraction decreases (from 10 to 4 vol%), Co lamellae width in the final foam also decreases (from 93 to 8 μm) while foam porosity increases (from 66 to 85%). A drop in solidification temperature (from −10 to −50 °C) decreases porosity (from 77 to 63%) and lamellae width (from 11 to 5 μm) at a constant 8 vol% slurry fraction. Finally, with increasing sintering time (for −10 °C solidification temperature and 8% slurry fraction), Co foam porosity decreases (from 77 to 68%) and lamella width strongly increases (from 10 to 59 μm), consistent with sintering-induced coalescence of lamellae. The Co foams exhibit high strength but relatively low stiffness as compared to simple theoretical models, consistent with internal Co lamella buckling. A uniform Co oxide layer is grown by oxidation to create an active coating on the Co lamellae useful for lithium-ion storage. A coin-cell test carried out on the oxidized Co foam demonstrates a capacity (1283 $mAhg^{-1}$) almost twice that of a control oxidized Co foil anode, owing to its considerably larger surface area. Finite-element analysis is used to compute stresses and plastic strain evolutions during the lithiation process to understand the effect of oxide layer thickness and roughness, and micropores within the Co lamellae.

1. Introduction

Because of its higher price as compared to iron- and nickel-based alloys, cobalt (Co) has found only niche structural applications [1,2] such as high-temperature superalloys [3], hard metal composites [4], and biocompatible alloy implants [2]. For non-structural applications, pure Co and Co-based alloys are widely used as catalysts (e.g., for electrochemical water oxidation) [3,4]. Co-based alloys are also considered potential alternatives to the scarce and expensive ruthenium- and iridium-based materials used in dye-sensitized solar cells (DSSCs) [5] and light-emitting electrochemical cells (LECs) [6] owing to their excellent physical, chemical, and mechanical properties. Co is also used, in its oxide forms, in functional applications in catalysts, magnetic storage devices, supercapacitors, lithium-ion batteries (LIBs), and sensors [7,8]. For the above applications, cobalt (in pure, alloyed or oxidize form) with fine, interconnected porosity or channels can be used as an advanced functional "platform" material because of their high specific surface area, light weight, high toughness, high gas and liquid permeability, reduced thermal and electrical conductivity (compared to its bulk counterpart), and high stiffness- (and strength-) to-weight ratios [9–12].

The ice-templating method (also known as freeze-casting) can produce porous structures via simple, low-cost, scalable processing steps where powder slurry freezing followed by freeze drying is combined with powder sintering, as shown in Fig. 1a. When, as shown in Fig. 1b, the powder slurry is solidified directionally on the cold bottom surface of a mold, vertical colonies of parallel solid dendrites grow along the direction of the thermal gradient pushing the powder between the growing dendrites and creating powder-packed regions. When water is used as the carrier for the slurry,

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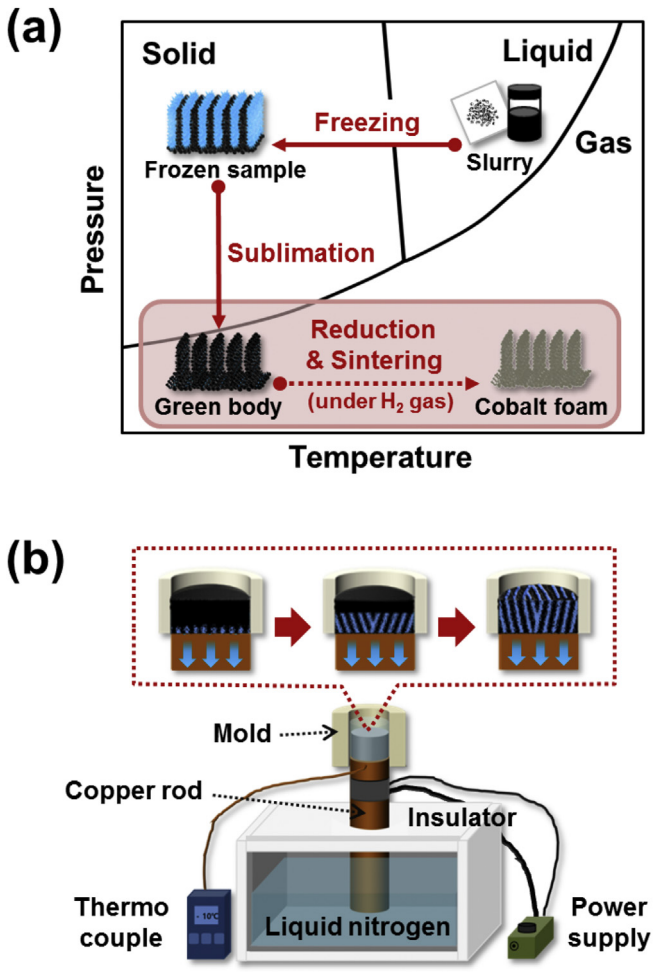

Fig. 1. (a) Schematic phase diagram of water illustrating phase changes in the liquid aqueous slurry during the ice-templating and sintering processes and (b) schematic illustration of ice-templating device and directional slurry freezing process.

highly anisotropic ice crystals (dendrites) grow along the thermal gradient. In a typical situation, the ice crystal growth occurs much faster along the "a" axis parallel to the thermal gradient than along the "c" axis perpendicular to the thermal gradient; however, the ice-crystal growth mechanism can be more complex in some situations. For example, the c-axis can also be parallel to the thermal gradient with the inclusion of an additive, which can affect the solidification parameters of the material system, such as the viscosity, surface tension, pH, freezing temperature, and interactions between the particles in suspension [13]. As the ice dendrites continuously grow along the temperature gradient, the solidification front velocity progressively decreases as it moves away from the mold bottom maintained at a constant temperature (as in a general set-up) and creates a microstructural gradient (e.g., with their thickness increasing to some extent), resulting in the formation of a structure composed of vertical lamellae of pure ice interspersed with regions rich in powders (Fig. S1) [14–16]. After full solidification, the ice dendrites are sublimated leaving directional pores, replicating the dendrites, surrounded by lamellae of packed powders. These are densified during a sintering step, thus forming a dense, three-dimensional porous material with elongated and aligned pores replicating the ice dendritic structure [14–26].

Ice templating has so far not only been applied to Co or its alloys, but a variety of porous ceramics and porous metals have been processed by the method [14–26], using for the latter metallic powders (titanium) [18,23] or oxide powders that are chemically reduced to metal (copper [16], iron [26], nickel [24], and tungsten [27]) after the freeze-casting step. The ice-templating process can be used to tailor the size, porosity, orientation, and shape of pores with relative ease by controlling the particle characteristics, powder content in the slurry, slurry solidification direction and velocity, and sintering time and temperature [14,19,21,25]. Due to their affordability and ease of fabrication, ice-templated porous metals, with their unique open directional structures with large surface areas, dense lamellae, and good mechanical properties, show promising potential for use as structural materials, as well as functional materials such as biomaterials, catalysts, sensors, and electrodes [14].

Although several forms of Co have been manufactured and reported for use in functional applications in the form of foil, nanopowder, nanowire, 3D-printed porous architecture [28], and sintered powder [29], we describe here for the first time the fabrication and structure of porous Co with a well-defined lamellar structure obtained by optimizing the primary processing parameters for the ice-templating process. We synthesize a porous green body using Co oxide (Co_3O_4) powders, and then reduce and sintere it to produce porous metallic Co. This study discusses the effects of powder slurry fraction, slurry solidification temperature and sintering time on the morphology of the synthesized Co foams. The compressive mechanical properties of selected Co foam samples are measured and compared with theoretical models.

Additionally, a representative Co foam, after thermal oxidation to form a Co oxide layer on its surfaces, is demonstrated as an anode of LIBs. This is because Co oxides, such as Co_3O_4 and CoO, are well known as high-capacity anode electrode materials for LIBs [30–34]. Finite element analysis (FEA) is then applied to examine the stress state developed in the Co/Co oxide foam during (de)lithiation associated with (dis)charging.

2. Experimental procedures

2.1. Sample preparation

A powder slurry was created by suspending 4 to 12.5 vol% Co oxide (Co_3O_4) nanoparticles (size ~30 nm, 99.9% purity, Inframat Advanced Materials, USA) in 5 ml deionized water, and 6.5 wt% polyvinyl alcohol (PVA, Sigma-Aldrich Co., USA, fraction calculated with respect to the Co_3O_4 powder) was added as a binder. The slurry was homogenized by a combination of stirring and sonication lasting ~150 min at ambient temperature, and then poured into a Teflon mold (20 mm inner diameter, 21 mm outer diameter, 25 mm height) whose bottom surface was a copper rod cooled at its lower end with liquid nitrogen. Using a resistive heater along the length of the rod, the temperature of its upper surface (forming the bottom of the mold) was maintained at −10, −30, or −50 °C. The strong thermal gradient within the slurry after pouring led to the vertical growth of ice crystals and rejection of suspended oxide particles to interdendritic space. The fully solidified slurry with a height of 14 mm was then sublimated, in a vacuum, at −88 °C for 24 h in a freeze dryer (Operon, FDU−7003, Republic of Korea), resulting in an oxide green body with directional pores replicating the sublimated dendrites. This green body was heated in a tube furnace, under a flowing Ar-5% H_2 gas mixture, to two consecutive temperatures: (a) 550 °C for 4 h to remove the binder and chemically reduce Co_3O_4 to Co and (b) 900 °C for 1.5, 2.5, or 4 h to sinter the metallic Co. Heating and cooling rates were 5 and 3 °C min^{-1}, respectively.

In a first series of experiments (sintering time control), slurries with 8 vol% Co_3O_4 powder were directionally solidified at a fixed copper rod temperature of −10 °C. After freeze drying and pre-