



In situ fabrication of cellular architecture on silver metals using methane/oxygen gas mixture and its application for energy storage

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ABSTRACT

Cellular metals with a large surface-to-volume ratio and excellent electrical conductivity have attracted great attention due to their wide application. However, the existing processes for fabrication of cellular metallic structures are generally complex and dependent on the sacrificial materials or templates, and therefore, it is highly desirable to develop a facile process. Herein, we propose a novel gas-assisted reconstruction strategy for in situ fabrication of micron-porous architectures on Ag precursor metal using a CH₄/O₂ gas mixture at 750 °C. The obtained results indicate that large-area and clean, porous Ag architectures are successfully created through the treatment in CH₄/O₂ gas. The formation of cellular structure is mainly due to the simultaneous diffusion of H₂, CO and O₂ into Ag bulk and fast reaction at elevated temperatures. The process is clean and applicable to creation of porous architectures (from surface texturing to 3-D cellular structure) on Ag metal, avoiding the use of sacrificial materials or templates. Furthermore, we have demonstrated that the formed micron-porous Ag sheet with large effective area, high electrical conductivity can be directly used as a free-standing electrode for electrochemical supercapacitors with a high capacitance.

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1. Introduction

Porous metals with a cellular architecture have attracted great attention for their wide application in catalysis [1], electrode [2,3], sensor [4], optical components [5], and so on, due to their novel physical and chemical properties. Therefore, there is a continued interest in the discovery of new technologies to process porous metals, such as direct foaming of liquid metals [6], sintering of metal powder slurry [7], electro-deposition [8], template method [9,10] and dealloying [5,11,12].

Silver (Ag) metal possesses remarkably high electrical conductivity with lower cost than other precious metals (Au and Pt) [3]. Therefore, porous Ag has been considered as desirable material for various practical applications in cathodic reduction catalysis [3],

efficient filtration system [13], surface enhanced Raman spectroscopy (SERS) [5], and electrochemical supercapacitors [14]. To date, the research on the preparation of porous Ag is mainly focused on chemical/electrochemical dealloying of different Ag alloy systems such as Mg-Ca-Ag [14], Al-Ag [15], Zn-Ag [16], and Mg-Ag [17] in acid or alkali solutions. Template method is another way to obtain porous Ag, which involves the dissolution of soluble salt nanoparticles [10]. However, these technologies for preparing porous Ag mostly involve introduction of additional components such as metal components (Al, Zn, Mg and Ca), and hazards of corrosive agents. Furthermore, complex and time-consuming multiple processing steps are needed for the dealloying process [5,11,12]. Moreover, it is difficult to form a uniform cellular structure of pure Ag metal on a large scale using the dealloying process, due to its poor pore formation ability and intrinsic low chemical stability [15,16].

Researchers have reported that gaseous oxygen (O₂) and hydrogen (H₂) have high solubility and fast diffusivity in the Ag metal at elevated temperatures [18–22]. For example, the

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diffusivities of H and O at 700 °C are $2.17 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ and $9.26 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, respectively, significantly greater than that of self grain boundary ($2.17 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) [22]. It was found that the structure of solid Ag was sensitive to these oxidizing (O_2) and reducing (H_2) gas environments at higher temperatures. For example, faceting of Ag surface was observed with a high oxygen content at ~ 800 °C when Ag was used as pin interconnect for solid oxide fuel cells (SOFC), while no structural change was observed in a reducing atmosphere [23]. Furthermore, small pores were observed on Ag surface when it is served as a sealing material for SOFC, which is simultaneously exposed to oxidizing (air) and reducing environments (H_2) at 600–800 °C [21,22]. Singh et al. first found that when an Ag tube (with a wall thickness of 0.25 mm) was exposed to $\text{H}_2/3\% \text{ H}_2\text{O}$ (inside the tube) and air (outside the tube) at 700 °C for 100 h, the inner walls were full of voids or pores [21]. On the contrary, no voids or pores were detected after both sides of the Ag tube were exposed to ambient air. They pointed out that the formation of pores is related to the simultaneous dissolution of O_2 from the cathode side and H_2 from the anode side into the bulk of Ag, which combine to form H_2O vapour. As the internal pressure is gradually built up, the gaseous H_2O will eventually escape from the Ag solid, producing the pores as observed [21].

However, in 2009 Akhtar et al. found that the porosity of Ag wire was distinct when it was employed as a current collector of cathode for micro-tubular single chamber SOFC (SC-SOFC) exposed in a methane/air mixture at 750 °C [24]. After the continuous operation for ~ 100 h, a fully porous structure of Ag (looking like nanowires) was present, but there was a lack of detailed discussion for the formation mechanism. Recently, we have studied the structural stability of solid Ag in CH_4/O_2 gas mixture under SC-SOFC conditions in an operating temperature range of 650–750 °C, with a CH_4 -to- O_2 ratio (R_{mix}) from 1 to 2. Our results indicated that the simultaneous diffusion of H_2 , CO and O_2 into Ag bulk and subsequent reaction result in the formation of gaseous H_2O and CO_2 , leading to rapid structural change of Ag. We observed that the presence of Ni/yttria-stabilized zirconia (YSZ) catalyst, high operating temperature and oxygen-rich atmosphere promote the oxidation of CH_4 in the CH_4/O_2 mixture, accelerating the pore formation process in Ag. Therefore, Ag is not a perfect material of choice for operating in hydrocarbon-air mixed gas, especially at the anode side.

Thus from the viewpoint of application in SOFC, significant pore formation is the mechanism of structural degradation of Ag samples under either a dual-environment or single chamber environment [21,22,24,25]. Little attention has been paid to the feasibility of applying the gas treatment approach in creating useful cellular architectures of Ag metal. Herein, we design a mixed gas-assisted reconstruction strategy to in situ create cellular structures in solid Ag metals using a proper CH_4/O_2 mixture ($R_{\text{mix}} = 2$) at 750 °C, which is facile and independent on additional components and processing steps. The formed micron-porous Ag sheet (MPAS) with a large internal surface, high electrical conductivity and fast mass transport channels holds great promise as three-dimensional porous electrodes for the applications in high-efficiency energy storage.

2. Experimental

2.1. Fabrication of cellular architectures on Ag metal

Purchased Ag wires (99.9%, 0.3 mm diameter, Kunming Institute of Precious Metals, China) and Ag sheets (99.9%, 0.1 mm thickness, Sinopharm Chemical Reagent Co., Ltd, China) were used. The as-received Ag samples were cleaned using an ultrasonic method before treatment. During this process, these Ag samples were

prepared and cleaned carefully to prevent any external forces to form internal stress and defects in the Ag precursors [25]. Based on the previous report [25], the Ni-YSZ catalyst could promote partial oxidation of CH_4 , accelerating the pore formation process. Therefore, the commercial NiO (Inco, Canada) and YSZ (TZ-8Y, Tosoh Corp, Japan) were mixed in an agate mortar at a weight ratio of 5:5, and subsequently reduced in H_2 at 750 °C for 2 h to form the typical Ni-YSZ catalyst. Both the Ni-YSZ catalyst and Ag samples were put in the center of a quartz tube with an inner diameter of 22 mm. A K-type thermocouple was in contact with the outer surface of the quartz tube, providing feedback signal to the temperature controller. The experimental setup was described in our early publications [25,26]. The tube with the Ni-YSZ and Ag samples was arranged in a furnace and heated to the designated temperatures in pure argon. Afterward, the gas mixture composing of 133 ml min^{-1} CH_4 , 67 ml min^{-1} O_2 and 100 ml min^{-1} Ar was fed to the Ni-YSZ and Ag samples. The fuel-to-oxygen ratio (R_{mix}) was fixed at 2 to ensure the mechanical integrity of Ag samples during the treatment process [25]. The flow rate of each gas was controlled using mass flow controllers (MFCs, Seven-Star Huachuang D08-4D/2 M). Finally, the samples were cooled to room temperature under Ar atmosphere.

2.2. Catalytic activity test and materials characterizations

The catalytic activity of the Ni-YSZ catalyst and Ag sample for methane partial oxidation was evaluated in continuous flow tubular quartz reactor at atmospheric pressure. These samples were placed into the middle of the quartz tube reactor with an inner diameter of 8.0 mm. The inlet gas was composed of 33 mL min^{-1} CH_4 , 17 mL min^{-1} O_2 and 50 mL min^{-1} Ar (33 vol.% CH_4 -17 vol.% O_2 -50 vol.% Ar). The effluent gas was connected to an on-line LC-D100 mass spectrometry (Ametek, USA) for compositional analysis.

A scanning electron microscope (Hitachi SU800, Japan) with an X-ray energy-dispersive spectroscope was used to characterize the microstructure and elemental changes of the Ag samples. The phase of the Ag samples was examined by X-ray diffraction (XRD, Rigaku D/max 2200, Japan) and Raman spectroscopy (Renishaw, 532 nm laser).

2.3. Electrochemical measurement

Cyclic voltammetry (CV) of the as-prepared Ag samples was investigated on an electrochemical station (Shanghai CH Instrument CO., China) by a three-electrode configuration in a KOH (1 M) aqueous electrolyte, where Pt and Hg/HgO (1 M KOH filling solution) were used as counter and reference electrodes, respectively. The galvanostatic charge/discharge (GCD) was carried out using the Neware equipment (Shenzhen, China). The applied potential window of CV and GCD was set from 0 V to 0.5 V.

2.4. Calculation

The specific (areal) capacitance can be calculated from the CV and GCD curves according to the equations below:

$$C = \frac{\int i(V)dV}{Sv\Delta V} \quad (1)$$

$$C = \frac{I\Delta t}{S\Delta V} \quad (2)$$

Where C is the specific capacitance of the materials, v is the scan rate, ΔV is the potential window in the CV and discharge process, i

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