

Nanoporous silver for electrocatalysis application in alkaline fuel cells

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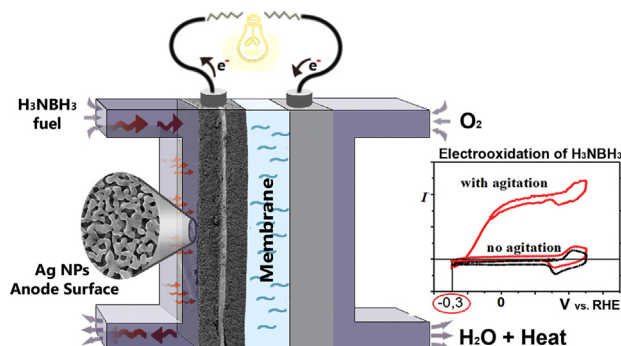
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HIGHLIGHTS

- Nanoporous silver is obtained via dealloying of Cu₃Si phase from the crystalline precursor.
- Bulk thin middle layer of nanoporous foil reinforces its mechanical integrity.
- Pores of <100 nm and high surface area of 5 m²/g is advantageous for catalytic applications.
- Designed material is successfully tested for applications in Direct Ammonia-Borane Fuel Cell as porous anodic catalyst.
- Materials show very high stability and lower onset voltage comparing to H₂-fed fuel cell.

GRAPHICAL ABSTRACT



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ABSTRACT

Self-supporting porous silver foils with an average pore size <100 nm were produced from a crystalline silver-based ternary alloy as a precursor by removing second phases present in the silver matrix. The final Ag-based porous foil shows good mechanical properties when comparing to its previous amorphous analogues. Its activity for direct electrochemical oxidation of ammonia-borane (AB), a fuel of interest for direct liquid fuel cells, has been investigated in alkaline media. The material exhibits promising electrochemical properties in long-term operation; indeed, material composition and nanostructure remain similar after 15,000 cyclic-voltammeteries between -0.3 and 0.5 V vs. RHE in a 0.1 M NaOH + 5 mM AB solution thermostated at 25 °C. Nanoporous materials, and in particular nanoporous silver, can therefore represent a relevant choice as anode in direct ammonia-borane fuel cell.

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1. Introduction

With the crescent global warming due to greenhouse gas emissions, the political and environmental climates are increasingly affected, and the demand for alternative fuels becomes unquestionably clear.

Hydrogen arises as a clean-energy option, generating only water after burning or electrooxidation. However, current technologies for hydrogen production, storage and transportation still require several shortcomings to be solved, for instance, green origin of the mother fuel (at present H₂ is processed from fossil fuel for >95% of its production) safety, energy-density, efficiency and cost.

Chemical hydrogen storage, in which hydrogen covalently bonded to molecules is released in gaseous form through (catalyzed) chemical reactions, offers a promising future for hydrogen storage and distribution. Considering the US Department of Energy target for the entire system weight (9.0 wt% H) [1,2], the compound ammonia-borane (H₃NBH₃, AB), with a molecular weight of 30.9 g/mol and an inherent capacity of 19.6 wt% H₂, is an obvious prime candidate as hydrogen storage compound. Solution and solid-state thermal dehydrogenation [3–5], as well as acid-catalyzed dehydrocoupling [6], have been reported for hydrogen production from amine-boranes. Transition-metal-catalyzed dehydrogenation reactions have only recently been described in the literature [7–11]. Precious noble metal catalysts (platinum-group metals - PGM) are active for AB dehydrocoupling at room temperature with catalyst loadings as low as 0.5 mol% [5].

Nevertheless, the above methodologies still suffer some drawbacks, which limit their utilization. PGMs are too expensive and poorly available. As such, PGM nanoparticles are usually supported on carbon black, which are of difficult manipulation and are not so good electron conductors. Finally, the degradation of these catalyst materials is another issue: noble metal nanoparticles were recently found highly instable in strong alkaline solutions [12–14].

Ammonia-borane is chemically stable in an alkaline medium [15] and its direct oxidation in Alkaline Fuel Cells (AFCs) can solve many of those issues. Indeed, AFCs present many advantages: for instance, the kinetics of many complex reactions is non-negligibly improved in an alkaline medium, and several metals (or metal oxides) are both active and stable in alkaline media (spreading the possibilities for material candidates to be used as electrodes) [16].

More importantly, by using an appropriate catalyst, the direct electrooxidation of ammonia-borane can initiate below the hydrogen oxidation potential [17] (<0 V vs. RHE, and as low as –0.3 V vs. RHE [18]), enhancing the energy efficiency of a Direct Ammonia-Borane Fuel Cell (DABFC) versus a hydrogen fuel cell fed after catalytic decomposition of borane fuels (in other words, the same number of electrons can be generated, but at much lower electrode potential). As such, the DABFC technology represents an interesting solution, in principle capable both of storing chemical energy and releasing it on demand with a reasonable efficiency and power density. Strong efforts have been realized to develop and improve AB oxidation catalysts [15,19–21] and use them in (hopefully efficient and economically viable) DABFC [18].

Given that both Zadick et al. [12,13] and Olu et al. [18] have brought evidences of the huge instability of platinum, and to a lesser extent of palladium nanoparticles supported on high surface area carbon in alkaline medium, the present research aims to develop cheaper and more abundant alternative catalysts for the electrochemical oxidation amine-boranes and their valorization in DABFC. In doing so, attention is paid to the catalyst durability and stability of performance. Silver in the form of nanoparticles, agglomerates, clusters and porous substances has already been widely used as catalysts in fuel cells and electrochemical actuators [22–25], in particular recently for the electrooxidation of borohydride compounds [26–30]. In that regards, nanoporous silver materials was evaluated as a potential anode catalyst for the DABFC.

There are many ways to elaborate metal-based porous catalysts. For instance, dissolution, a simple but powerful elaboration strategy, is commonly used to obtain nanoporous metallic systems. As a result of dissolution, less-noble elements are selectively leached from the mother alloy, driving a reorganization of nobler elements of the alloy-electrolyte interface into a 3-dimensional pattern [31,32]. This is commonly constituted by the noblest element, but it can also have a multi-elemental composition [33–36]. Crystalline alloys preserve their original

microstructure after leaching: in other words, each grain becomes a crystal surrounded by a porous structure [37].

Nanoporous metals find their application as sensors, [38,39] catalysts [23,35,36,40–42], actuators [43,44], SERS substrates [42,45,46], and often combine advantageous structural properties with bactericidal and biocompatible ones [47–49]. Due to their very high specific surface area, nanoporous metals may present excellent catalytic properties for a series of important heterogeneous reactions, because of interconnected ligaments and 3D channels that may allow free transport of medium molecules and electrons [50–52].

Since the development of the field of nanoporous metals, a great number of works has been dedicated to the design of noble metal-based nanoporous architected structures, among which silver plays an important role [46,53–56]. Among others, nanoporous silver (NPS) was obtained in the group of De Hosson by dealloying Al from the amorphous Ag–Al precursor alloy [57]. Another interesting “clean” method of its fabrication was recently suggested by the group of T. Zhang when amorphous Ag–Ca foils were simply immersed in water to remove calcium atoms [55].

In the previous work by M. Zhang et al. [56] was reported the fabrication of a porous silver material with a submicron pore size. The precursor of the given work was an amorphous Ag_{38.75}Cu_{38.75}Si_{22.5} alloy that was exposed to an appropriate etching condition in order to eliminate Cu and Si atoms, leaving a single Ag porous carcass. Homogeneous distribution of elements in the amorphous state is a key to obtain the fine ultimate porous architecture upon reorganization of Ag atoms while etching; on the contrary, when in crystalline precursors are used, the final characteristic features are determined by the phases present in the ingot [24]. However, in spite of the finely architected structure, the bulk material produced from the amorphous precursor [56] did not possess sufficient mechanical integrity and robustness to allow any further experiments revealing its advantages, particularly in the field of catalysis where good failure resistance is required.

The general aim of our work is firstly to approach the structural composition of previously elaborated NPS foils so as to enhance their mechanical characteristics. In the present paper, we make a step beyond and characterize a porous silver material from an electrochemical viewpoint, in particular versus the direct electrooxidation reaction of ammonia-borane in an alkaline medium, a model reaction of interest towards the development of direct alkaline fuel cells. Besides, the stability of this material is also investigated in accelerated stress-test operation.

2. Experimental section

2.1. Materials' preparation and characterization

A set of Ag-based polycrystalline alloys of composition Ag_{38.75}Cu_{38.75}Si_{22.5} were prepared by arc melting of pure Ag, Cu and Si (99.99% purity, Alfa Aesar) in helium atmosphere. To homogenize the alloy, minimum 5 additional melting steps were made before the rapid solidification casting of the material on the copper wheel. Foils with thicknesses ranging between 20 and 60 μm were produced by varying the rotating speed of the copper wheel. After analyzing X-ray diffraction (XRD) results and preliminary chemical treatment tests of the obtained samples, the 20 μm thick foils showed finer porous architecture and were chosen for further careful characterization and ammonia-borane electrooxidation tests.

The XRD patterns of as-spun and dealloyed components were obtained using a PANalytical X'Pert Pro MRD instrument with a copper (Kα) radiation (0.051°/step, in variable mode).

The microstructures and chemical compositions of the ribbons were observed using a high-resolution ZEISS Ultra 55 scanning electron microscope equipped with a field emission gun (FEG-SEM) and energy-dispersive X-ray analyzer (EDS).

To analyze the pore size of the as-dealloyed ribbons an imaging tool ImageJ [58] was used.

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