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High-performance HER on magnetron-sputtered nanometric Nb films on porous silicon substrates

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ABSTRACT

The hydrogen evolution reaction (HER) stands out as one of the most extensively studied electrocatalytic reactions in literature. Herein, niobium has been tested for the first time for the catalysis of the HER in the form of nanometer-thick-films. The deposition of 5, 10, and 50 nm-thick Nb thin films onto both smooth and porous silicon substrates, the latter ones with mesopores with mean diameters of 13 nm and 7 nm, respectively, has been successfully achieved using magnetron sputtering, a highly precise and controllable technique allowing a very efficient deposition of Nb films. After the sputtering deposition, the samples were examined by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDAX) analyses which confirmed the purity and uniformity of the Nb coating on all samples. Electrochemical tests revealed top-notch performance, with almost negligible onset potentials (es. 80 mV vs. RHE) and low Tafel slopes (es. 30 mV/dec), thereby paving the way for the future development of cutting-edge devices.

1. Introduction

Human activities, mainly due to the emission of greenhouse gases, are irremediably causing damage to the environment, promoting negative consequences for human well-being, economies, and societies, and inflicting distress and damage upon nature and human communities [1–3]. In the need for new renewable energy sources, green hydrogen is currently considered a key element, as well as the hydrogen evolution reaction one of the most significant ways to produce it [4–11]. This process is particularly interesting since it can exploit excess energy generated from intermittent and regional renewable sources to provide hydrogen, which can be effectively stored, and only water as a by-product. The cycle, from hydrogen storage to clean energy production, highlights the crucial potential of hydrogen as an energy carrier and the possibility of facilitating the transition to a more sustainable, low-carbon energy system [3]. For this reason, many catalysts and devices have been tested toward HER [12–16]. However, some metals,

such as niobium, have been very little explored [17,18], although promising and never in the form of thin films.

Considering that the HER is confined to the electrode's surfaces, it is logical to evaluate it in nano-film configurations as a natural progression. Indeed, since hydrogen evolution is a heterogeneous catalytic reaction, the morphology of the thin and ultrathin films allows for to enhancement of the intrinsic properties of niobium [19]. Nanometer-thick-films also have economic intrinsic advantages, rather than employed in bulk form. Furthermore, its tenacity against acid corrosion is extensively documented, primarily ascribed to the rapid oxidation of its surface into Nb₂O₅, acting as a defensive layer and safeguarding it from any corrosive attacks [17,20,21]. As discussed by H. Nady et al. [17], the oxide layer makes the sample very stable and efficient in acid environments [22].

The deposition of niobium thin films can be achieved with high precision and notable control via magnetron sputtering [23,24]. Magnetron sputtering is a physical vapor deposition (PVD) technique in

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