



# Self-activated anodic nanoporous stainless steel electrocatalysts with high durability for the hydrogen evolution reaction

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## ABSTRACT

Stainless steel-based electrocatalysts have attracted tremendous attention as alternatives to precious noble metal-based catalysts for renewable energy research, as they are readily available and inexpensive. Herein, self-activated anodic nanoporous stainless steel is demonstrated as a highly efficient and durable electrode with improved catalytic performance for the hydrogen evolution reaction. Etched and anodized stainless steel (EASS) is prepared by anodization using etched stainless steel 304 foil with a rough surface, followed by thermal annealing. Due to its extremely high surface area, evolved oxygen vacancies, and excellent durability for 100 h at  $100 \text{ mA cm}^{-2}$ , EASS that has been annealed in an  $\text{Ar}/\text{H}_2$  atmosphere (EASS- $\text{Ar}/\text{H}_2$ ) exhibits an overpotential of 370 mV, lower than that of pristine etched stainless steel electrode (466 mV) in 1 M KOH aqueous solution. In contrast, EASS annealed in air (EASS-air) displays no catalytic activity. Interestingly, the overpotential of EASS- $\text{Ar}/\text{H}_2$  is further reduced to 244 mV after 10,000 cycles of linear sweep voltammetry by self-activation due to the generation of Ni-rich hydroxide with increasing oxygen vacancies.

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## 1. Introduction

Clean and renewable energy sources must be developed in order to address the growing number of energy issues arising from the unsustainable use of fossil fuels and the severe environment consequences of their use [1–3]. One critical challenge is to transform diverse renewable energy sources, such as wind, wave power, and solar energy into energy that can be distributed and used without loss [4,5].

Hydrogen energy is a promising alternative to fossil fuels for efficient energy production and storage [6–9]. Currently, hydrogen is produced in industry by steam reforming of fossil fuels, which produces large quantities of the greenhouse gas,  $\text{CO}_2$ , as a by-product. Electrochemical water splitting is an ideal environmentally friendly approach for hydrogen production, as it converts water, a safe and readily available resource, into an ideal form of chemical energy [10–12]. Electrochemical water splitting consists of coupled two half-reactions: the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), which occur simultaneously at an applied theoretical voltage of 1.23 V [13–15]. However, an overpotential is required to compensate potential loss resulting from sluggish reaction kinetics [6,16–20]. To this end, the use of electrocatalysts can

accelerate reaction kinetics and lower the energy barrier of water dissociation, thereby reducing the required overpotential. State-of-the-art noble electrocatalysts, such as Pt for HER [17,18] and Ru/Ir-based compounds for OER [19,20], have been widely studied for reducing the overpotential for electrochemical water splitting. However, the high costs and scarcity of noble metals severely limit their use for industrialization. Therefore, noble metal-free electrocatalysts have been explored as inexpensive, abundant, stable, and highly active alternatives to noble electrocatalysts. Transition metal sulfides, phosphides, oxides, nitrides, and carbides have been proposed as highly efficient water splitting catalysts [16].

Stainless steel is rich in transition metal elements such as Fe and Ni, two abundant, inexpensive elements that commonly act as active centers in electrochemical reactions [21–24]. However, conventional stainless steel is rarely effective for electrochemical water splitting, due to its chemically inert surface and its lack of active sites, originating from a small surface area. Therefore, it is imperative to develop an efficient route to improve the electrocatalytic performance of stainless steel and elucidate its working mechanism [25–30].

In this study, we use (electro)chemistry and thermal annealing to obtain a stainless steel based-catalyst with enhanced electrochemical performance. This novel process comprises several steps: (i) chemical etching by hydrochloric acid, (ii) electrochemical anodization in an ethylene glycol-based solution, and (iii) thermal annealing under various atmospheres. Chemical etching results in

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