



# Three-dimensional electrode coatings for hydrogen production manufactured by combined atmospheric and suspension plasma spray



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## ABSTRACT

Nickel-based electrode coatings for hydrogen production by alkaline water electrolysis were prepared using atmospheric plasma spraying (APS) and suspension plasma spraying (SPS) methods. To enhance the active surface area of the electrodes and obtain various levels of surface roughness, three-dimensional fin arrays were fabricated by masking the substrates with mesh screens during APS deposition. Subsequently, SPS top coatings were deposited on the fin-structured electrodes. The electrodes were then characterized by studying their surface microstructure, topography, roughness and electrochemical performance. The highest electrocatalytic activity with the exchange current density of  $1.8 \times 10^{-3} \text{ A/cm}^2$  and overpotential ( $\eta_{250}$ ) of  $-339 \pm 15 \text{ mV}$  was obtained for the electrode coated by the combined APS–SPS method using the mesh screen with the smaller opening size. The high activity of this electrode is mainly attributed to the unique surface structure formed by deposition of particles through the fine mesh screen and impacting at different angles on the fin geometry.

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## 1. Introduction

High purity hydrogen produced by alkaline water electrolysis is considered to be a promising replacement for fossil derivative fuels [1]. In recent years, water electrolysis has gained wide attention due to the increasing concerns about greenhouse gas emissions and the growing demand for green and renewable energy resources [1,2]. The produced hydrogen can be stored and used later as an energy carrier in fuel cells or combustion engines [3]. Nonetheless, water electrolysis is still not used for large-scale hydrogen production, as it remains costly due to its high electricity consumption [4,5]. Therefore, the main challenge is to improve the energy efficiency of the electrolysis process by minimizing the overpotentials of the cathodic (hydrogen evolution) and anodic (oxygen evolution) reactions [5,6]. One approach to reduce the overpotential of the hydrogen evolution reaction (HER) is employing electrocatalysts with high intrinsic activities [7,8]. Nickel is widely used as the electrode material for the HER because it is abundant, has high electrocatalytic activity among non-noble metals and is stable in alkaline solutions [9–12]. Moreover, physical properties of an electrode such as its surface structure have also substantial effect on its catalytic activity. An enhanced electrode surface area provides a larger electrode/electrolyte interface, and thus, more reaction sites for hydrogen adsorption/desorption [5,8–10,13]. The surface properties depend substantially on the method used to prepare the electrodes.

Among various thermal spraying methods that have been used to manufacture nickel-based electrodes, atmospheric plasma spray (APS)

has shown its capability in development of micron and nano-structured active electrode coatings for the HER [14–19]. In this process, the sprayed particles melt and accelerate towards the substrate within the high temperature plasma jet. Subsequently, the deposition layers are formed by impact and flattening of the molten droplets on the substrate at high velocities [20]. Nevertheless, submicron- and nanosized particles cannot be used directly in APS due to the injection difficulties they may impose to the spray system. Suspension plasma spray (SPS) based on the injection of a liquid carrier was developed to overcome this problem. SPS process includes injection of a suspension of solid particles into the plasma jet, atomization and evaporation of the liquid phase, and then melting, acceleration, impact and deposition of the particles on a substrate similar to what was explained for the conventional APS process [21–23].

In our previous work, it was shown that electrodes with high activities could be developed by combination of the two APS and SPS methods [17,18]. In this combined method, few SPS layers were deposited on already APS coated electrodes. The superior electrochemical properties of the electrodes were mainly related to their large effective surface areas with unique hierarchical microstructures. The dual micron/submicron-sized surface features enhanced the electrode activity by promoting surface accessibility to the electrolyte, providing more reaction sites for hydrogen adsorption and facilitating hydrogen bubble release from the surface [17,18].

In the current study, we present a novel approach for further improvement of the electrochemical properties of the electrodes for the HER. In this work, the surfaces of the electrodes were engineered by fabricating different macro- and microscopic levels of surface roughness when applying the combined APS–SPS coatings. For this purpose,

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the substrates were masked by wire mesh screens during the coating processes and the possibility of forming three-dimensional fin arrays on their top surfaces, through the small openings of the mesh screens, was investigated. Previously, Cormier et al. [24] developed such near net shaped fin arrays by coating aluminum powder through the wire mesh screens using cold spray for manufacturing compact heat exchangers. By producing electrode coatings using the combined APS–SPS method and the mesh screens a considerable improvement in electrode overpotential is expected, as the developed structural features enhance the electrode/electrolyte contact area at both macro- and microscopic scales. The performance of the electrodes was studied by investigating their microstructural properties and steady-state polarization curves.

## 2. Materials and methods

Commercially available powders namely nickel Metco 56C-NS (Oerlikon Metco, USA) and nickel oxide FCM NiO-F (fuelcellmaterials.com, USA) were used to coat Inconel 600 substrate coupons with the surface dimensions of  $25 \times 25 \text{ mm}^2$ . The particle size distribution of the starting powders was determined to be between 45 and  $90 \mu\text{m}$  with D50 of  $69 \mu\text{m}$  and 100 nm to  $11 \mu\text{m}$  with D50 of 730 nm for nickel and nickel oxide, respectively, using a laser diffraction particle size analyzer (Malvern Instruments Ltd., England) [17].

Nickel electrode coatings were prepared using a 40 kW Sulzer Metco 3 MB atmospheric plasma spray gun mounted on a 6-axis robotic arm. The electrodes were coated at two distinct stages. At the first stage, the substrate coupons were masked by plain woven steel wire mesh screens (McMaster-Carr, USA) with two different mesh sizes. The mesh screens were varied in their wire diameter and opening size from one to another. A schematic view of a mesh screen that was used is illustrated in Fig. 1. Table 1 shows the wire diameter and opening size for each mesh. For both samples, the standoff distance from the mesh to the substrate was fixed at 1 mm. The masked coupons were then coated under similar coating conditions by 40 passes of APS using nickel powder. Fig. 2 shows a schematic view of the APS process and the developed coating using a mesh screen.

At the second stage, the mesh screens were removed of the APS coated electrodes from the first stage, and the samples were coated by additional passes of SPS using nickel oxide suspension. The suspension was prepared by mixing 10 wt.% of nickel oxide with 1 wt.% of polyvinylpyrrolidone (PVP) as the dispersing agent in ethanol. The details of suspension preparation and the injection setup for the SPS process is explained in our previous work [14]. Table 2 shows the plasma spraying parameters used in APS and SPS coating processes. The parameters were selected based on our previous results [14,17]. The samples were named according to Table 3 throughout this work.

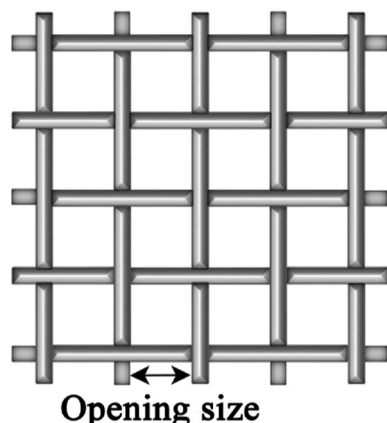


Fig. 1. A schematic view of a mesh screen used in the coating processes.

The velocity and temperature of the inflight particles were measured by a DPV-eVOLUTION particle characterization system (Tecnar Automation Ltd., Canada) for the APS process at the spray distance. The substrate temperature was recorded by an Infrared camera (FLIR A320, FLIR Systems Inc., USA) and a pyrometer (M67S, LumaSense Technologies, USA) during APS and SPS, respectively. As the coatings were oxidized due to the high flame temperature of APS at atmospheric conditions and deposition of nickel oxide in SPS, the electrodes needed to be reduced. Oxygen reduction of the samples was carried out in a tube furnace by hydrogen gas at  $650 \text{ }^\circ\text{C}$  for 1 h, with  $2 \text{ }^\circ\text{C}/\text{min}$  heating and cooling rates.

To study the cross-sections of the coatings, the samples were cut using a precision cut-off machine (Secotom-15, Struers, Denmark), cold mounted in epoxy and then polished by standard metallographic procedures to a final finish of  $0.05 \mu\text{m}$ . An optical microscope was then used to study the cross-sections of the samples. A 3-D Confocal Laser Scanning Microscope (CLSM) (LEXT-OLS4000, Olympus Corporation, Japan) with a Z-axis height resolution of 10 nm and a lateral X–Y resolution of 120 nm was used for three dimensional topography imaging of the coatings and to evaluate the roughness of the sprayed samples. The top surface morphology of the coatings was observed by a scanning electron microscope (SEM) (S-3400 N, Hitachi High Technologies America, Inc., USA) operating at 15 kV.

A standard three-electrode cell was used for the electrochemical measurements. In this setup, the coated samples as the working electrode, a platinum wire as the counter electrode and an Hg/HgO reference electrode saturated in 1 M KOH ( $-0.924 \text{ V}$  vs. Hg/HgO) were fixed in a Pyrex cell containing a 1 M NaOH electrolytic solution. The electrolyte was bubbled with nitrogen throughout the whole measurements to remove its oxygen content. All measurements were carried out at room temperature ( $25 \text{ }^\circ\text{C}$ ). Before each measurement, surface oxide layers were removed by pre-polarization of the working electrode at  $-1.6 \text{ V}$  vs. Hg/HgO for 1800 s. Tafel polarization curves in the current range of  $10 \mu\text{A}$  to 1 A were obtained using a SRS potentiostat (EC301, Stanford Research Systems, Inc., USA). The kinetic parameters including the Tafel slope,  $b$ , and exchange current density,  $j_0$ , were determined from extrapolation of the linear part of the Tafel curves to the equilibrium potential. The overpotential of the electrodes was measured at an applied current density of  $250 \text{ mA}/\text{cm}^2$  in the galvanostatic mode.

## 3. Results and discussion

### 3.1. Microstructural characterization

#### 3.1.1. Surface morphology

Fig. 3 shows SEM overview images of the coatings for electrodes CM and FM. The fins present trapezoidal prism geometry in CM, whereas they are dome shaped in FM. Both coatings present highly porous structures, specifically in the grooves formed under the mesh wires as well as on the slopes of the fins.

SEM micrographs of the top surfaces of the fins are presented in Fig. 4a and b for electrodes CM and FM, respectively. It can be seen that the microstructure of electrode CM is comprised of a combination of flattened splats, fragmented splats and resolidified droplets. The diameter of some of the splats are as large as  $100 \mu\text{m}$  suggesting that the largest particles were fully melted under the spraying conditions. For electrode FM, only few particles are deposited on the top surface of the fins due to smaller size of the wire mesh openings. For this sample, clogging of some of the mesh screen openings by nickel powder was noted after deposition of 40 passes, which could be related to its small opening size compared to the particle size that was used. However, no deterioration of the mesh wires or clogging of the mesh screen openings could be observed in the coarse mesh during the coating process, which can be related to its larger mesh opening size and higher wire diameter. For both coatings the substrate temperature during the coating process was measured in the

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