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Fabrication of nickel electrode coatings by combination of atmospheric and suspension plasma spray processes

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ABSTRACT

Atmospheric plasma spray and suspension plasma spray were presented as two promising methods for manufacturing nickel cathode electrode coatings for alkaline water electrolysis, using micron- and submicron-sized powders, respectively. A combination of both processes was also successfully utilized as a novel method by deposition of a suspension plasma sprayed layer on an atmospheric plasma sprayed one to develop high performance electrodes. The coated electrodes were then characterized in terms of their microstructure, surface topography, wettability and steady state polarization curves. The highest electrocatalytic activity was obtained for an electrode coated by the combined method with the exchange current density and overpotential (η_{250}) values of 6.2×10^{-4} A/cm^2 and -386 mV, respectively. The high activity of this electrode was attributed to its large specific surface area with a high surface roughness value ($S_a = 14.4$ μm) comprising a multiscale micron/submicron-sized surface structure. It is expected that the dual microstructure of this electrode in addition to its superhydrophilic behaviour (with contact angles below 10°) enhances the activity by providing more reaction sites for hydrogen adsorption, promoting the diffusive mass transport of the reactants, and facilitating hydrogen bubble ascension from the pores.

1. Introduction

In recent years, production of high purity hydrogen by alkaline water electrolysis as a clean energy carrier has gained significant attention due to the increasingly damaging effects of the greenhouse gas emissions and environmental pollution [1]. However, high electricity consumption of the electrolysis process has made this method costly for large scale hydrogen production, and therefore, its efficiency needs to be increased by reducing the hydrogen production overpotentials [2,3]. For this purpose, two methods have been proposed including manufacturing electrodes using intrinsic active materials and enhancing the electrode active surface area [3–5]. Nickel is widely used as the electrode material for the hydrogen evolution reaction (HER), because it has relatively high catalytic activity and is inexpensive compared to noble metals such as platinum [6,7]. Among various electrode production techniques, plasma spray has demonstrated its capability to manufacture nickel based electrode coatings with large surface areas and high roughness values [8–13].

In atmospheric plasma spray (APS), the plasma plume is generated by ionization of a jet of argon or nitrogen as the primary gas mixed with hydrogen or helium as the secondary gas by a strong electric arc generated between the cathode and the anode. Micron size particles with an average particle size of 10 to 100 μm are introduced into the high velocity, high temperature plasma jet. Subsequently, coatings are generated by acceleration, impact, flattering and deposition of molten and semi-molten particles on the surface of a substrate [14].

It has been shown that manufacturing electrodes with nanostructured surfaces significantly enhances their electrocatalytic activity, which could be related to their unique electronic properties and presence of a large density of surface defects, such as grain boundaries [15,16]. However, submicron and nanosized particles cannot be used directly in plasma spraying due to their low flowability and injection difficulties they cause in the spraying system. Suspension plasma spray (SPS), invented in the mid-1990s in the University of Sherbrooke, Canada, is an alternative to the conventional plasma spray for injection of submicron and nanosized particles using a liquid feedstock [17]. In a SPS process, the suspension undergoes fragmentation and vaporization of the droplets after its injection into the plasma jet (Fig. 1). The particles are then accelerated, partially or fully melted depending on their residence time within the plasma flow and form a coating upon impact on the substrate [18,19]. Since smaller particles decelerate faster and undergo extremely rapid heating and cooling rates, the spraying distances are usually shorter in SPS (4 to 6 cm) compared to APS (8 to 12 cm) [18].

It is worth noting that a fraction of the inner surface of the coatings that could be efficiently used for hydrogen production could easily get blocked by the hydrogen bubbles at very small pore sizes of the developed coating. This could consequently reduce the electrocatalytic activity by imposing additional electrical resistances and ohmic losses, and

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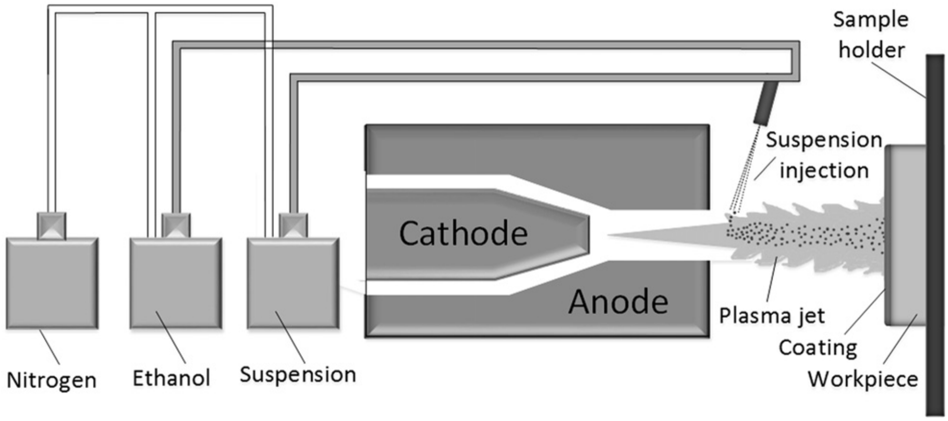

Fig. 1. Schematic view of the SPS process.

thus, decrease the rate of the HER [20,21]. Therefore, controlling the size of the pores is one of the most important factors that should be considered during deposition of the nanostructured coatings.

Preliminary results on combining the APS and SPS methods for manufacturing electrodes with hybrid micron and submicron-sized surface structures were reported by the authors recently [13]. In the current study, further optimization of the HER efficiency was carried out by investigating the influence of the number of the passes deposited by SPS on top of the APS coated electrodes. Such unique microstructures and surface morphologies developed by the combined APS–SPS method are expected to provide enhanced electrode surface areas, and overcome the hydrogen bubble blockage problem within the pores. Electrocatalytic activity of the produced electrodes was determined for the HER, and it was compared to the activities of those electrodes produced by solely APS and SPS coating processes.

2. Experimental

2.1. Materials and spray conditions

The starting powders used to deposit the electrode coatings included nickel Metco 56C-NS (Oerlikon Metco, USA), and nickel oxide FCM NiO-F (fuelcellmaterials.com, USA) for APS and SPS coating processes, respectively. Fig. 2 shows the particle morphology of both powders.

Particle size distribution of both powders was determined by a laser diffraction particle size analyser (Malvern Instruments Ltd., England) using a 300 mm lens. The results, illustrated in Fig. 3, show a distribution width of 45 to 90 μm for the micron sized nickel powder and from 100 nm to 11 μm for the submicron sized nickel oxide powder. The distribution widths of D10, D50, and D90 were measured to be 60, 69, and 78 μm for nickel and 0.20, 0.73 and 4 μm for nickel oxide powders, respectively.

Suspensions for the SPS were prepared by mixing of 10 wt.% of nickel oxide powder with 1 wt.% of polyvinylpyrrolidone (PVP) as dispersing agent in ethanol. The injection setup for the SPS process was developed in-house and described in detail in a previous work [12]. A 200 μm internal diameter tube was used to radially inject the suspension into the plasma jet.

All coatings were deposited using a 40 kW Sulzer Metco 3MB atmospheric plasma spray gun mounted on a six-axis robotic arm. Argon and hydrogen were used as the primary and the secondary plasma gases, respectively, whereas nitrogen was used as the carrier gas for injecting dry powders in APS. The depositions were carried out onto rectangular Inconel 600 coupons with a surface area of 645 mm^2.

Atmospheric and suspension plasma sprayed electrodes were prepared by deposition of 8 and 25 passes on the substrate coupons, respectively. To take advantage of a multiscale surface structure, three additional electrodes were prepared by suspension plasma spraying of thin layer coatings on top of the APS deposited electrodes. To determine the optimum number of the passes required to deposit by SPS for maximizing the efficiency of the HER, 3, 6 and 10 passes were deposited by SPS. For simplicity, these three electrodes were named S3, S6 and S10, respectively, throughout this paper.

The plasma spraying parameters used for deposition of APS and SPS coated electrodes, listed in Table 1, were selected based on the methodology reported previously [12,13]. The parameters were obtained by optimization of the processes towards maximizing the surface area of the coatings while having a good adhesion to the substrate.

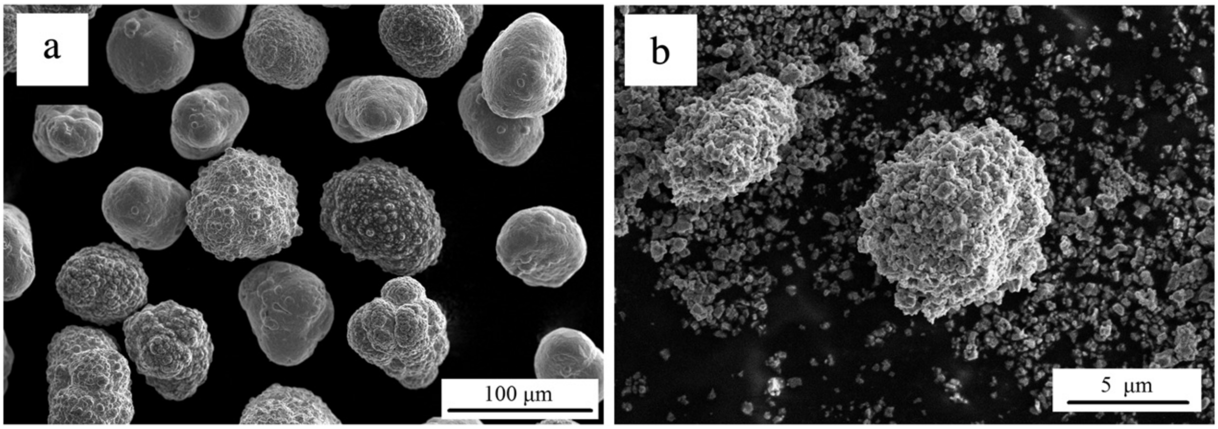

Fig. 2. SEM morphology of the precursor powders, (a) nickel and (b) nickel oxide.