

Article

Stable Surface Technology for HER Electrodes

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Abstract: With the rapid increase in energy consumption worldwide, the development of renewable and alternative energy sources can sustain long-term development in the energy field. Hydrogen (H₂), which is one of the clean chemical fuels, has the highest weight energy density and its combustion byproduct is only water. Among the various methods of producing hydrogen source, water electrolysis is a process that can effectively produce H₂. However, it is difficult for commercialization of water electrolysis for H₂ production due to the high cost and low abundance of noble metal-based cathodic electrode used for highly efficiency. Several studies have been conducted to reduce noble metal loading and/or completely replace them with other materials to overcome these obstacles. Among them, stainless steel contains many components of transition metals (Ni, Cr, Co) but have sluggish reaction kinetics and small active surface area. In this study, the problem of stainless steel was to be solved by utilizing the electrocatalytic properties of silver nanoparticles on the electrode surface, and electrodes were easily fabricated through the electrodeposition process. In addition, the surface shape, elemental properties, and HER activity of the electrode was analyzed by comparing it with the commercialized silver nanoparticle-coated invasive electrodes from Inanos (Inano-Ag-IE) through the plasma coating process. As a result, silver nanoparticle-coated conventional electrode (Ag-CE) fabricated through electrodeposition confirmed high HER activity and stability. However, the Inano-Ag-IE showed low HER activity as silver nanoparticles were not found. We encourage further research on the production process of such products for sustainable energy applications.

Keywords: water electrolysis; hydrogen evolution reaction; stainless steels; surface modification; silver nanoparticles



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1. Introduction

Over the past century, worldwide energy consumption has been rapidly increased due to the development of science and technology, population growth and fossil fuel exploitation [1–3]. The energy demand is expected to increase to around 583 exajoules (EJ) [2,4], and the continued surge in energy consumption raised the atmospheric carbon dioxide (CO₂) level to more than 410 ppm, seriously affecting Earth's ecosystem [3,5]. On the other hand, as human society develops, the world's energy consumption will increase even further; more than 80% of current energy consumption will still be obtained from conventional energy sources, e.g., coal, petroleum, oil, and natural gas [5]. Suppose we fail to prevent the continued surge in fossil energy consumption, in that case, global average temperature will rise, not only disrupting millions of lives around the world, but leading to massive global migration and conflict. Accordingly, more than 1260 climate laws have been enacted, including the Paris Agreement in 2015, to reduce energy consumption and CO₂ emissions worldwide. They are taking effective measures to avoid the effects of climate change [2,6]. Therefore, the development of renewable and alternative energy sources that can reduce current CO₂ emissions, solve energy problems and sustain long-term power generation is required urgently.

When utilized in a fuel cell for stationary, distributed, or transport applications, hydrogen (H_2) is one of the clean chemical fuels, which has the highest gravimetric energy density of approximately 120 MJ kg^{-1} , almost 3 times more than diesel (45.6 MJ kg^{-1}) or gasoline (46.4 MJ kg^{-1}) [7–9]. Additionally, H_2 has the advantage of clean combustion, in which the byproduct is only water without emitting CO_2 during the hydrogen combustion process [7]. However, most of the H_2 is currently being produced by steam-reforming resources that consume fossil fuels and emit CO_2 [10]. Therefore, H_2 generation from sustainable, renewable, and efficient technologies solves the present limitation to produce and play the key element for future energy development.

Water electrolysis, or electrochemical water splitting to produce hydrogen and oxygen, has long been considered a promising method for H_2 production. It was first reported in 1789, and consists of two half-cell reactions, the hydrogen evolution reaction (HER, $2H^+(aq) + 2e^- \rightarrow H_2(g)$) and the oxygen evolution reaction (OER, $2H_2O(l) \rightarrow 4e^- + 4H^+(aq) + O_2(g)$), which occur at the cathode and anode simultaneously [7,11]. Derivatives of the noble metal group, e.g., platinum (Pt), silver (Ag), gold (Au), etc., have been known as high-efficiency electrochemical catalysts for HER owing to their optimal hydrogen binding energy (HBE), Gibbs free energy for atomic hydrogen adsorption (ΔG_{H^*}), low activation energies for H_2 desorption from the surface, high exchange current density (j_0), and small Tafel slope [7]. However, the noble metal-comprised bulk electrodes have drawbacks for large-scale applications due to their high cost and scarcity, rendering H_2 generation difficult to commercially viable. As a result, many attempts have been made for the hydrogen evolution reaction (HER), in recent decades to reduce noble metal loading and/or fully substitute it, for example, with graphene, an excellent electrical conductor [12,13], or transition metal-based cathodic electrodes [14,15].

Stainless steel, which is widely employed as a conductive substrate for energy storage and electrocatalysis due to its high durability and low cost, is an attractive alloy material rich in transition metals such as iron (Fe), nickel (Ni), and chromium (Cr) [16]. Olivares-Ramírez et al. reported the HER performance on ordinary stainless steels [17]. They note that stainless steel works as the cathodic electrode for HER because of the highest composition of transition metals, which acts as an effective active site. Likewise, the transition metals of stainless steel act as active centers for electrochemical water splitting. However, ordinary stainless steel shows low electrochemical performance due to its sluggish reaction kinetics and lack of active sites, originating from a small surface area [16,17]. To improve these disadvantages of stainless steel, few works in the literature have been reported, such as an increase in the surface area through etching and anodization [16] or N,P co-doped carbon nanotubes coating [18].

One of the recent research paths for improving stainless steel-based cathodic electrodes is electrode modification using nanotechnology. In various fields, the performance is improved by utilizing electrode surface modification through functionalization such as graphene-modified [19], carbon nanotube tip [20], and gold-coated [21]. Especially, various studies showed that silver nanoparticles deposited or coated on other substrates have highly effective electrocatalytic activity for HER [22,23]. Moreover, as a noble metal element that is white in appearance with a glossy, soft and stretchy texture, silver has unusual optical, chemical, electrical and thermal properties [24]. Recently, the antimicrobial properties of silver nanoparticles have been identified and used in medical technology research applications [25–27].

Among the various attractive features of silver nanoparticles, there is therapeutic tool that utilizes an induced therapy effect. Inanos, a manufacturing company from Korea, was one of the companies to commercialize these silver nanoparticle-coated invasive electrodes. A single pack of this Inanos product contains eight silver nanoparticle-coated invasive electrodes ($0.30 \text{ mm} \times 40 \text{ mm}$), as shown in Figure S1. As claimed, this silver nanoparticle-coated electrode has excellent antibacterial, sterilization, deodorization, and functional characteristics. The patent discussed the capability of their product in quickly relieving

pain and breaking down body fat. The company received a Korean patent in 2005 and registered its discovery as a silver nanoparticle-coated invasive electrode [28].

As a research group with great interest in nanotechnology and its application field, we were intrigued by the effect of silver nanoparticles in electrocatalysts and inducing therapy. In addition, the commercialized Inanos silver nanoparticle-coated invasive electrode (Inanos-Ag-IE) was manufactured through a plasma coating process [28]. However, it has a complex process and high-cost problems, so it needs to be improved. In this research, we fabricated a silver nanoparticle-coated conventional electrode (Ag-CE) using electrochemical deposition, which has a simple process and low-cost technique than plasma coating. In addition, by analyzing the surface morphology, element composition and HER performance of each electrode sample, we discuss a stable surface technology for HER cathodic electrodes.

2. Results and Discussion

Figure 1 shows the surface morphologies of the three types of electrodes analyzed in this manuscript. Figure 1a shows a scanning electron microscope (SEM) image of the surface of the as-obtained conventional electrode (CE). We used CE to compare the surface morphology of the commercialized Inano-Ag-IE, as shown in Figure 1b. In Figure S2, Inanos produced their patented product, Inano-Ag-IE, and presented 1–5 μm optimized coating thickness through SEM analysis [28]. However, after purchasing Inano-Ag-IE products, we analyzed them with SEM, and it was found that the surface morphology of Inano-Ag-IE is similar to CE with no identifiable silver nanoparticles on the Inanos product surface. Additionally, we compared the surface morphology of Inano-Ag-IE with the electrodeposited silver nanoparticle-coating on the conventional electrode (Ag-CE). In Figure 1c, the lighter colored area on the surface of the Ag-CE sample is due to the silver coating. At a higher magnification, this silver coating on the electrode observed that it was made up of silver nanoparticles (Figure 1d). Compared to the commercialized Inano-Ag-IE, the silver coating on the Ag-CE is more evident. Thus, the silver nanoparticle coating on the electrode obtained from Inanos is not identifiable through SEM analysis.

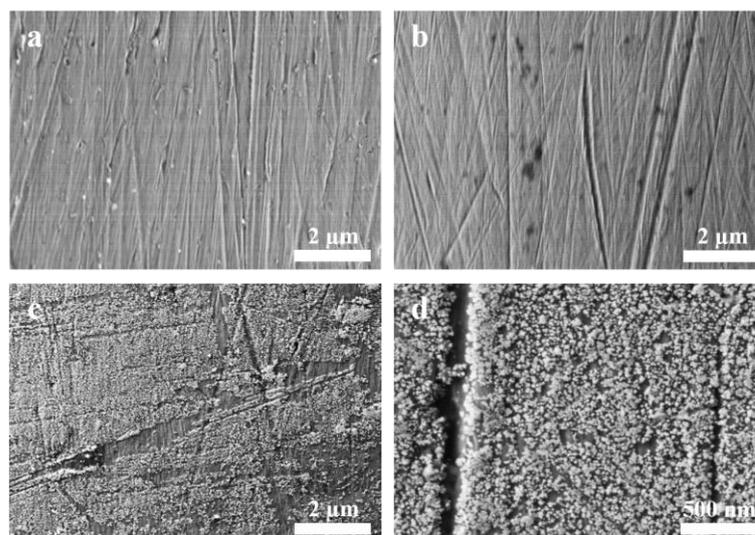


Figure 1. SEM images of (a) CE; (b) Inano-Ag-IE, and (c) Ag-CE electrode bodies obtained by our research group; (d) Enlarged image of Ag-CE electrode body.

Since the silver coating was not evident through SEM analysis, EDS analysis was performed to confirm the presence of silver on the surface of the electrodes. Comparison of elemental analysis spectra shows the similarity among the CE electrode body and handle (Figure 2a,b), and Inano-Ag-IE electrode body (Figure 2c), wherein both have no silver element detected. However, upon analysis of the Inano-Ag-CE handle, traces of the silver

nanoparticles were detected, as shown in Figure S3d. Meanwhile, energy-dispersive X-ray spectroscopy (EDS) data for the Ag-CE electrode body confirms the presence of silver on the surface of the electrode coated through electrodeposition (Figure 2e,f). Though small in quantity, the silver coating is still confirmed in the Ag-CE body since the uncoated CE body does not have any traces of silver.

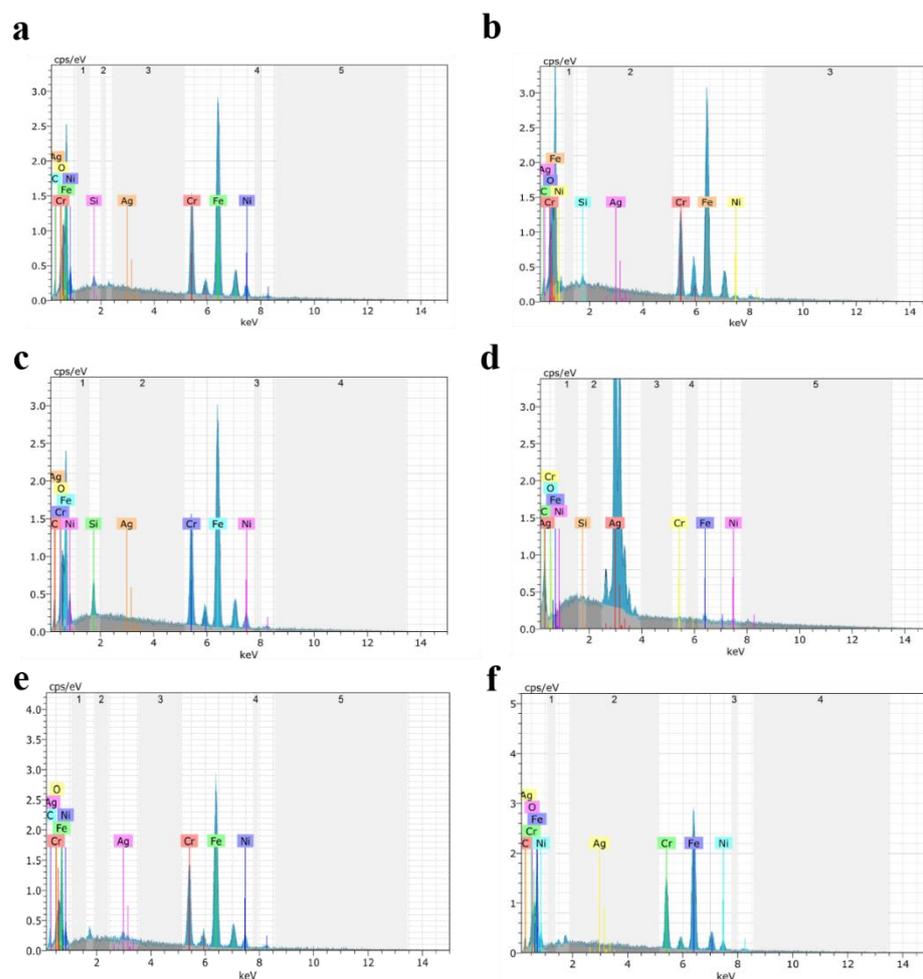


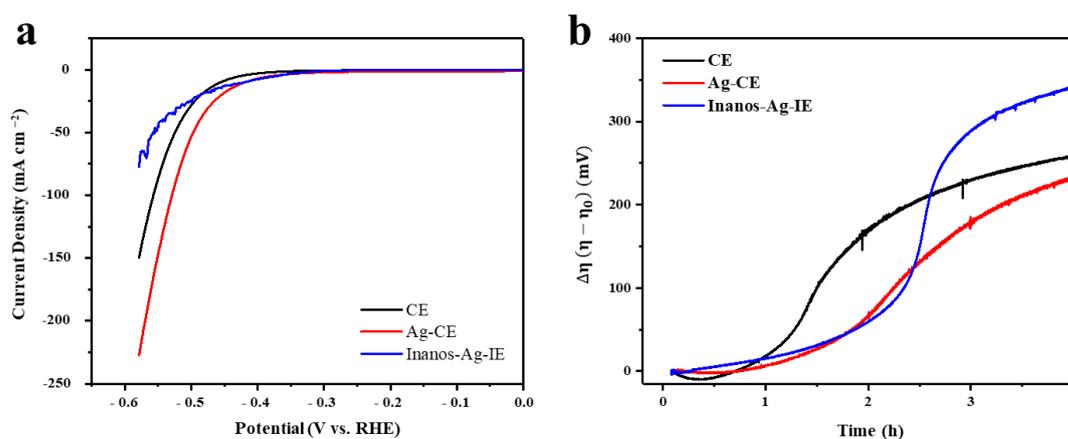
Figure 2. EDS spectra of (a) CE body; (b) CE handle; (c) Inano-Ag-IE body; (d) Inano-Ag-IE handle; (e) Ag-CE body, and (f) Ag-CE handle.

Table 1 lists the main elements detected by EDS from the electrode body and handle (Figure S3) of CE, Inano-Ag-IE, and Ag-CE samples. The majority of elements listed are the alloy components of the stainless steel electrode, i.e., Fe, C, Cr, Ni, and O. However, it is notable that the Inano-Ag-IE body has a more detectable silicon component compared to the other samples (Figure 2c and Table 1). This is assumed because of the structure of the silver coating, which is a combination of silver (Ag) and silica (SiO_2), as explained in the patent document (Figure S4).

Table 1. List of elements detected by EDS from the CE, Inano-Ag-IE, and Ag-CE samples, and their atomic weight percentage (at.%) per.

Element (at.%)	CE		Inano-Ag-IE		Ag-CE	
	Electrode Body	Electrode Handle	Electrode Body	Electrode Handle	Electrode Body	Electrode Handle
Iron	58.31	64.21	50.31	2.37	56.01	59.40
Carbon	15.08	17.53	21.32	8.15	19.73	14.13
Chromium	18.93	15.65	14.05	0.23	14.36	15.43
Nickel	5.19	1.63	5.90	0.88	7.59	7.59
Oxygen	1.46	0.21	6.12	0.62	1.76	3.45
Silicon	1.03	0.77	2.30	0.18	0.00	0.00
Silver	0.00	0.00	0.00	87.57	0.55	0.00

To confirm the electrochemical catalytic activity for HER of each sample, the analysis was performed through linear sweep voltammetry (LSV). LSV under negative potential in KOH electrolyte is a well-known technique for evaluating HER electrocatalytic activity [16,29,30]. CE, Ag-CE, and Inano-Ag-IE were measured by linear sweep voltammetry in 1M KOH (Figure 3a). As a result, the Ag-CE sample shows the highest cathodic current density in comparison to other samples. On the other hand, Inano-Ag-IE has a lower current density compared to Ag-CE. In addition, in the stability through chronopotentiometry (CP), overpotential changes of CE, Ag-CE, and Inanos-Ag-IE were 17.1%, 14.6%, and 22.0% compared to the initial values (Figure 3b). These results are influenced by the presence or absence of silver nanoparticles on the surface of each stainless steel-based electrode sample.

**Figure 3.** Electrochemical catalytic activity for HER: (a) Polarization curves and (b) Stability test for CE, Ag-CE, and Inano-Ag-IE.

From the above results, we were unable to detect the silver nanoparticles on the surface of the Inano-Ag-IE electrode body and could not confirm the characteristics of the electrode claimed in the patent [28]. Moreover, it is difficult to credit the patent for the electrodeposition technology of invasive electrodes through plasma coating that they proposed. However, the electrodeposition technique can be made more easily than the plasma coating proposed in the patent. It confirmed that silver nanoparticles are evenly distributed on the surface of the stainless steel electrode through SEM analysis in Figure 1c. In addition, the high activity and conductivity of silver nanoparticles can complement the disadvantages of stainless steel materials and, at the same time, have a high surface area [22,31,32]. As a result, it shows high HER activity and stability during the electrocatalytic reaction than conventional stainless steel electrodes.

3. Materials and Methods

3.1. Preparation of Commercialized Silver Nanoparticle-Coated Invasive Electrodes from Inanos (Inano-Ag-IE)

The silver nanoparticle-coated invasive electrode was investigated as obtained from Inanos. This company obtained a Korean patent in 2005, and all the information in this section is derived from the document, as mentioned earlier [28]. Their unprocessed invasive conventional electrode (SUS304 stainless steel, 0.30 mm diameter, 40 mm length) is prepared, and the process involved in coating the silver nanoparticles onto the electrode surface is explained in detail on the patent. Briefly, their process involves plasma coating of fine silver nanoparticles (1–5 nm) onto the electrode, repeated up to 4 times to achieve the desired coating of 1–5 μm thickness. There was no further processing of these samples before surface and elemental analysis.

3.2. Preparation of Silver Nanoparticle-Coated Conventional Electrodes (Ag-CE)

The conventional electrodes (SUS304 stainless steel, 0.18 mm diameter, 8 mm length) utilized in this investigation were purchased from Dong-bang Acupuncture Inc., Boryeong-si, Korea. These samples were coated with silver nanoparticles by electrodeposition. Silver nanoparticle electrodeposition was carried out in a two-electrode cell operating at 2.0 V, with a CE used as the cathode and carbon paper (Carbon and Fuel cell (CNL), Seoul, Korea, 3 mm \times 20 mm \times 0.042 mm) as the anode, and distance between the two electrodes was 1 cm. The electrolyte used for the electrodeposition process consisted of 0.02 wt.% AgNO_3 (99.0%, American Chemical Society (ACS) reagent, Sigma-Aldrich, St. Louis, MO, USA) and 2.0 vol.% DI water in ethylene glycol (Extra Pure, Daejung, Siheung-si, Korea). The optimal electrodeposition time used for this process is 75 s, based on the previous study [27]. After electrodeposition, the Ag-CEs were thoroughly washed with hot DI water (70 $^\circ\text{C}$) to remove any loosely attached nanoparticles and dried under nitrogen gas stream.

3.3. Characterization of Electrode Samples

Field Emission Scanning Electron Microscope (FE-SEM, Hitachi S-4800, Tokyo, Japan) operating at 3 kV and 10 μA was used to study the surface morphologies of the electrode samples. Elemental analysis was obtained using Energy Dispersive Spectroscopy (EDS, Bruker Co., Karlsruhe, Germany), operating at 15 kV and 10 μA with a 20.0 k magnification and a working distance of 15 mm.

3.4. Electrochemical Measurements for Hydrogen Evolution Reaction (HER)

All electrochemical measurements for hydrogen evolution reaction (HER) were carried out in 1.0 KOH electrolyte (85%, Extra Pure, Daejung, Siheung-si, Korea) using a three-electrode system by VSP potentiostat (Bio Logic, Seyssinet-Pariset, France). In a three-electrode system, a saturated calomel electrode (SCE), and Pt wire as reference electrode and counter electrode were used, respectively. The working electrodes were CE, Ag-CE, and Inano-Ag-IE electrodes. The HER activity of as-prepared electrodes was evaluated by linear sweep voltammetry (LSV) from -1.00 to -1.65 V vs. SCE with a 5 mV s^{-1} scan rate. Additionally, stability measurements were conducted by chronopotentiometry (CP) at constant 30 mA cm^{-2} for 4 h. Potential values were referenced to a reversible hydrogen electrode (RHE) by calculating with the following equation: $E_{\text{RHE}} = E_{\text{SCE}} + 0.244 + 0.0591 \times \text{pH}$ [16].

4. Conclusions

Based on the SEM and EDS data analysis of the commercialized silver nanoparticle-coated electrode from Inanos, there were no traces of silver on the surface of the electrode samples. We can confirm that this product does not uphold the patent description by which it is based upon. Moreover, Inanos-Ag-IE has a lower HER activity than other stainless steel-based electrodes. Meanwhile, it was confirmed that silver nanoparticles were distributed at high density on the surface of the stainless steel electrode through simple

electrodeposition. Silver nanoparticle-coated electrodes manufactured by electrodeposition not only complements the low active surface area and electrochemical performance of the conventional stainless steel electrodes but also has the advantage in that it can be manufactured easily and quickly. Additionally, Ag-CE show high HER activity and stability compared to Inano-Ag-IE. Therefore, the silver nanoparticle-coated stainless steel based-electrode fabricated by electrodeposition is expected to show high H₂ performance. We hope that this paper will encourage researchers to explore advances in nanotechnology and its application.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11060693/s1>, Figure S1: One pack of silver nanoparticle-coated invasive electrodes obtained from Inanos containing eight 0.30 mm × 40 mm electrodes, Figure S2: SEM images of Inanos silver nanoparticle-coated invasive electrodes (Inano-Ag-IE) provided by the patent which shows the (a) cross-sectional view and (b) top view of the silver nano-coating, Figure S3: SEM images of the samples used in EDS analysis: (a) electrode body and (b) handle, Figure S4: A three-dimensional structural diagram explaining the silver nanostructure of the coating of Inano-Ag-IE.

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