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Application of dense nano-thin platinum films for low-temperature solid oxide fuel cells by atomic layer deposition

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ABSTRACT

Nano-thin platinum (Pt) films with a dense microstructure for low-temperature solid oxide fuel cells (LT-SOFCs) were fabricated by atomic layer deposition (ALD) and were characterized in terms of their micro-structural properties and electrochemical performance. Pt thin films with a purity level of ~99% were achieved by controlling the O₂ pulsing time. The agglomeration behavior of the ALD Pt thin films was characterized by the annealing temperature, becoming extremely severe above 550 °C. An LT-SOFC with a 25 nm thick dense ALD Pt cathode layer exhibited a peak power density of ~110 mW/cm² at 450 °C.

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Introduction

The insufficient cell performance of low-temperature solid oxide fuel cells (LT-SOFCs) is mainly associated with the poor reaction kinetics of these cells at the electrode–electrolyte interface at considerably low operating temperatures (e.g., below 500 °C) [1]. In particular, the sluggish oxygen reduction reaction (ORR) at the cathode requires the use of electrode catalysts with high levels of the catalytic activity [2]. Platinum

(Pt) is the material that is most frequently used as the cathode material due to its excellent ORR activity, but its high price acts as a critical obstacle preventing the commercialization of LT-SOFCs [3]. For this reason, research on the development of non-Pt materials such as metal oxides, non-noble metals and carbon-based materials has been actively conducted by many groups [4–6]. However, at present, materials suitable as a replacement for Pt at the cathode have yet to be found.

On the other hand, catalytic reactions in fuel cells are limited to the triple-phase boundary (TPB), which is the

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electrode/electrolyte/gas interface [7]. This means that electrode catalysts with a very small amount of Pt can also generate moderate reaction kinetics if there are no current collecting issues. This cost-effective strategy, in fact, has been attempted by means of vacuum deposition techniques, which are capable of forming uniform thin films [8,9]. In particular, atomic layer deposition (ALD), derived from chemical vapor deposition (CVD), has unique strengths such as atomic-scale controllability and unprecedented “uniformity and conformality.” This approach has recently been actively applied to fabricate nano-thin Pt electrode catalysts capable of high catalytic activity [10–12]. Jiang et al. comparatively analyzed the material and electrochemical properties of ALD Pt thin films and porous Pt thin films created by physical vapor deposition (PVD) using a silicon-based free-standing SOFC platform [10]. Chao et al. investigated the electrochemical characteristics of bi-layered electrode catalysts composed of an ultra-thin ALD Pt catalytic layer and a PVD porous Pt current collecting layer [11]. Furthermore, Ahn et al. optimized the ALD cycle of Pt electrode catalysts in terms of the power density of pellet-based SOFCs without an additional current collecting layer [12].

Considering that Pt intrinsically has a relatively very high surface energy, it is commonly known that its agglomeration at high temperatures reduces TPB lengths, considerably deteriorating the reaction kinetics at electrode–electrolyte interfaces [13]. In addition, in terms of the surface energy unit (joule per area) of materials, nano-particles with relatively large surface areas inherently have higher surface energy levels than dense thin films [14]. However, these studies above on ALD Pt electrode catalysts mainly focused on the applicability of isolated (or networked) ALD Pt nano-particles as electrode catalysts for LT-SOFCs while considering the active fuel supply to the electrolyte. Therefore, such an issue indicates that Pt electrode catalysts which diffuse fuel with a dense microstructure need to be used, considering their agglomeration characteristics to ensure the thermal durability of the resulting LT-SOFCs. If a dense Pt electrode catalyst is too thick, the resulting LT-SOFCs will undergo poor mass transport through the electrode catalyst. However, several recent reports have found that gas diffusion is possible when the thickness of the Pt electrode catalyst is a few tenths of nanometer, following the formation of TPB [13].

In this study, a dense but nano-thin Pt film for use as an electrode catalyst for LT-SOFCs was fabricated by ALD and micro-structurally and electrochemically characterized. The purity of the ALD Pt film was controlled by changing the O₂ pulsing time. The ALD Pt thin film was annealed in an air atmosphere, replicating the operating conditions of the cathode, which was micro-structurally characterized. Considering that the fuel diffusion and thermal stability simultaneously have to be guaranteed, the authors limited the thickness of ALD Pt electrode catalysts to approximately 25 nm, which is close to the minimum thickness required to form a dense microstructure [10]. To investigate the electrochemical properties, the ALD Pt thin film was used as a cathode electrode catalyst in LT-SOFCs supported by anodic aluminum oxide (AAO) with a PVD porous palladium (Pd) current collecting layer. The initial cell performance was evaluated as a function of the operating temperature, and electrochemical impedance spectroscopy (EIS) results were analyzed in terms of the dwell time.

Experimental methods

Thin film fabrication

The ALD Pt thin films were fabricated using a showerhead-type commercial CVD machine (Atomic Premium, CN1, Korea) capable of holding a six-inch wafer. The ALD chamber with a load-lock wafer handler was pumped by a dry pump to a base pressure of 20 mTorr. Trimethyl(methylcyclopentadienyl)platinum(IV) (Sigma Aldrich, USA) was used as the Pt precursor. The temperatures of the stage and the chamber wall were set to 350 °C and 110 °C, respectively. The temperatures of the electro-polished stainless steel (SS) canister and the SS piping system were 50 °C and 70 °C, respectively. The growth rate of the films was very slow at less than 0.01 Å/cycle when the SS canister temperature was below 30 °C. High purity O₂ gas at a flow rate of 300 standard cubic centimeters per minute (sccm) was used as the reactant and high purity argon (Ar) gas flowing at 300 sccm was used as the carrier gas. The Pt films were deposited by repeating the sequence of a precursor pulse (3 s), purging (10 s), a reactant pulse (1–3 s) and purging (10 s).

The PVD Pt and Pd thin films were deposited using a commercial sputtering machine (A-Tech System Ltd., Korea) equipped with a customized rotating unit. The target-to-substrate distance was 75 nm. A sample support to reduce growth rate deviation was rotated at 4 rpm. A 99.99% purity Pt and a 99.99% purity Pd target was used to deposit the PVD Pt and Pd thin films, respectively. Dense Pt thin films were deposited at 5 mTorr in an Ar atmosphere. The porous Pd thin films were deposited at 50 mTorr in an Ar atmosphere. The direct current (DC) power of the sputtering gun used was 200 W, and the Ar gas purity was 99.9999%.

Thin film characterization

X-ray photoelectron spectroscopy (XPS) was conducted to investigate the chemical properties using AXIS His (Kratos Analytical, Japan), and any possible surface contaminants were eliminated by means of 150 eV Ar-ion etching for 30 s prior to the analysis. X-ray reflectometry (XRR) was utilized to estimate the film density using the X'Pert Pro (PANalytical, Netherland) instrument with Cu K α radiation in the grazing incidence scan mode. The four-point probing method was used to measure the sheet resistance using the CMT-SR1000N instrument (AIT, Korea), and a correction factor was applied to each sample to remove the effect of the shape and size. The error range of the sheet resistance was plus or minus less than five percentage point. Focused ion beam and field emission scanning electron microscopy (FIB/FE-SEM) analysis was conducted to investigate the microstructures using a Quanta 3D FEG (FEI Company, Netherland), and a Pt layer a few nanometers thick was coated onto each sample to prevent the thin films from being etched by the FE-SEM imaging process.

Electrochemical evaluations

Test cells were attached to the custom-made H₂ feeding chamber using a ceramic adhesive (CP4010, Aremco Products,

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