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Atomic layer deposition of ruthenium surface-coating on porous platinum catalysts for high-performance direct ethanol solid oxide fuel cells

Heon Jae Jeong, Jun Woo Kim, Dong Young Jang, Joon Hyung Shim*

Renewable Energy System Laboratory, School of Mechanical Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 136-713, Republic of Korea

HIGHLIGHTS

- Bi-metallic electrodes were synthesized by ALD Ru coating on sputtered Pt mesh.
- Island-growth of ALD Ru was observed on the Pt surface.
- High ethanol-fuel-cell performance was achieved with Pt/ALD Ru 50 below 500 °C.
- Carbon content was significantly reduced due to bi-functional catalysis by Pt/Ru.

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ABSTRACT

Pt–Ru bi-metallic catalysts are synthesized by atomic layer deposition (ALD) of Ru surface-coating on sputtered Pt mesh. The catalysts are evaluated in direct ethanol solid oxide fuel cells (DESOFCs) in the temperature range of 300–500 °C. Island-growth of the ALD Ru coating is confirmed by transmission electron microscopy and X-ray photoelectron spectroscopy (XPS) analyses. The performance of the DESOFCs is evaluated based on the current–voltage output and electrochemical impedance spectroscopy. Genuine reduction of the polarization impedance, and enhanced power output with improved surface kinetics are achieved with the optimized ALD Ru surface-coating compared to bare Pt. The chemical composition of the Pt/ALD Ru electrode surface after fuel cell operation is analyzed via XPS. Enhanced cell performance is clearly achieved, attributed to the effective Pt/ALD Ru bi-metallic catalysis, including oxidation of C═O by Ru, and de-protonation of ethanol and cleavage of C–C bonds by Pt, as supported by surface morphology analysis which confirms formation of a large amount of carbon on bare Pt after the ethanol-fuel-cell test.

1. Introduction

Solid oxide fuel cells (SOFCs) are regarded as the most promising distributed power generation systems, offering the merits of being operable at elevated temperatures, having high conversion efficiency in combination with thermal devices, and fuel flexibility [1–4]. The recent thrust has been towards utilizing SOFCs for small and mobile systems [5–7]. A key requirement for miniaturizing SOFC systems is downsizing of the fuel storage devices and processors [5–7]. Towards this end, SOFCs that directly utilize liquid fuels such as alcohols may be useful as the next-generation fuel cell systems. Alcohol fuels, such as methanol and ethanol, have many advantages relative to gaseous fuels such as hydrogen, such as higher volumetric energy densities, easy storage, and transportation as liquid-state fuel [8,9]. Ethanol is particularly attractive because of its lower toxicity compared to methanol and its facile synthesis, since ethanol can be readily produced from a variety of sugar-containing bio-resources [9,10]. Consequently, the development of high-performance polymeric direct ethanol fuel cells (DEFCs) [9–12] has been actively pursued, and several recent studies have focused on the development of direct ethanol SOFCs (DESOFCs) including cells with Ni-based anodes while these systems are operable at relatively high temperatures and

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* Corresponding author.
E-mail addresses: mypleasure86@korea.ac.kr (H.J. Jeong), kim8604wo@korea.ac.kr (J.W. Kim), jadoyu@korea.ac.kr (D.Y. Jang), shimm@korea.ac.kr (J.H. Shim).

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there is a severe carbon deposition problem [13–18]. Therefore, there has been continuous effort to develop effective fuel catalyst for DEFCs or DESOFCs operable at low temperatures [11–15]. Bare Pt is recognized as the most effective catalyst for de-protonation of ethanol. However, the ethanol de-protonation process generates carbon monoxide (CO) that tends to passivate the Pt catalyst surface, where CO is hardly converted into CO_2 even in the presence of oxygen or water. To resolve this issue, Ru and Sn that can form hydroxyl groups on the catalyst surface and effectively oxidize CO have been added to the Pt catalyst with relative success [11,12].

Multiple approaches have been applied to the synthesis of high-performance bi-metallic catalysts for fuel cells [19,20]. Among the developed protocols, atomic layer deposition (ALD) has earned distinction as a novel process for fabrication of nano-alloy films. ALD can be used to produce uniform film layers on substrates with complex morphologies, with control of the thickness and composition on the sub-nanometer scale [21–26]. ALD has been successfully applied to the coating of ultrathin (thickness <10 nm) catalytic films or nano-particles conformal on electrodes [27–31]. Heterogeneous metal surface alloys fabricated by ALD are reportedly effective for methanol oxidation [31,32]. However, to the best of our knowledge, there is no report focusing on the use of the ALD catalyst for ethanol oxidation or any literature reporting working fuel cells employing these materials.

In this study, ALD is applied to deposition of Ru on the surface of Pt mesh, and the resulting Pt-ALD Ru surface alloys are evaluated as catalysts for DESOFCs. The optimal surface composition of Pt and Ru is determined by preparation of SOFC samples using various Ru ALD cycles. The electrode performance is investigated in terms of the fuel cell current–voltage (I–V) outputs and impedances. The micromorphology and chemical composition of the anode surface is also analyzed before and after cell operation.

2. Experimental

2.1. Preparation of DESOFC samples with Pt/ALD Ru bi-metallic electrodes

The DESOFC samples were prepared as electrolyte-supported fuel cells. $Gd_{0.1}Ce_{0.9}O_{2-\delta}$ (GDC) pellets were used as the electrolyte, and were synthesized from commercial GDC powder (Rhodia) via the uniaxial pressing method. The compressed green pellets were sintered at 1450 °C for 10 h at a heating rate of 2.4 °C min^{-1} in air. The sintered GDC pellets were polished to dimensions of 350 μm thick with a diameter of 1 cm. The pellets were identified as dense and polycrystalline, as confirmed by X-ray diffraction (XRD, D/MAX-2500V/PC, Rigaku, Korea University) and field emission-scanning electron microscopy (FE-SEM, S-4800, Hitachi, Korea University). As supporting electrodes for the DESOFC samples, porous Pt mesh was prepared via DC sputtering at 90 mTorr and 100 W in Ar gas atmosphere for 10 min. The morphology of the sputtered Pt, a porous and columnar mesh structure, is shown in the Supporting Information (Fig. S1). On the cathode side, the sputtered Pt mesh was circular with a diameter of 0.35 cm. On the anode side, the Pt mesh covered the entire pellet surface for good contact with the gold gasket seal. ALD of Ru was performed on the porous Pt mesh at the anode side for 50–200 cycles. Consequently, the bare porous Pt mesh was used as the cathode for all test samples, while the bare Pt and ALD Ru-treated Pt meshes were used as the anode. For ALD of Ru, bis(ethylcyclopentadienyl) ruthenium(II) ($Ru(EtCp)_2$) (UP Chem.) precursor and pure oxygen (99.9%) oxidant were utilized in a thermal ALD system (ICOT Company Inc.). During ALD, the substrate was heated at 320 °C, which has been reported

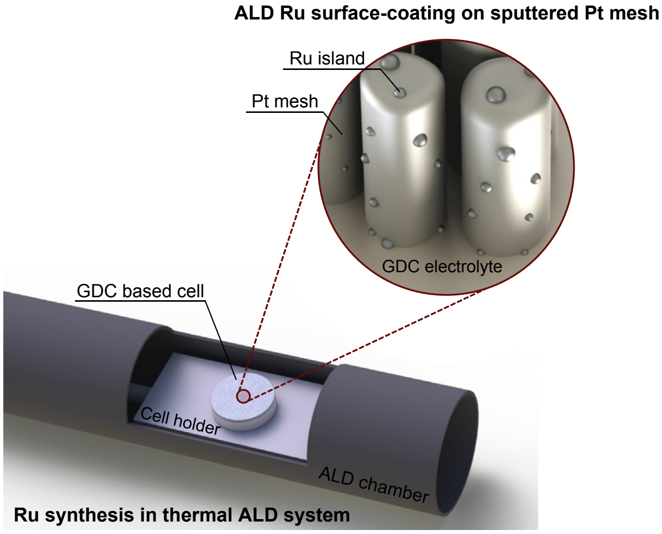
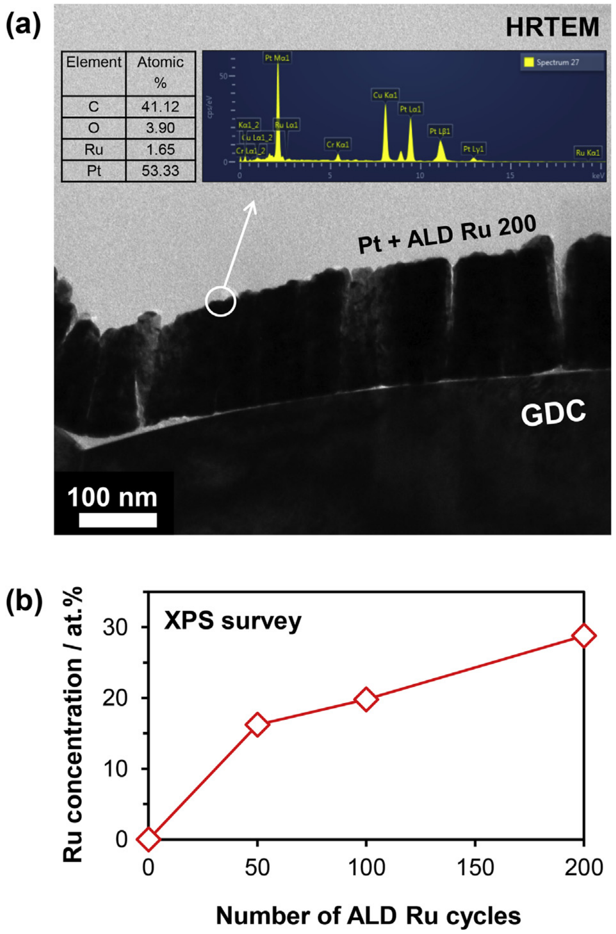


Fig. 1. Schematics of synthesis of Pt/ALD Ru bi-metallic catalysts on SOFC electrolyte pellets.



Element	Atomic %
C	41.12
O	3.90
Ru	1.65
Pt	53.33

Fig. 2. (a) Cross-sectional TEM image of Pt/ALD Ru 200 on GDC pellets; inset shows EDS compositional analysis. (b) Ru content on the surface of Pt and Pt/ALD Ru 50-200 samples, measured by XPS survey scanning.