

Ethanol electro-oxidation on Pd nanoparticle-decorated CeO₂ nanostructures

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ABSTRACT

Direct alcohol fuel cells stand out as a good alternative to fossil fuels in terms of energy efficiency. In this study, electrochemical synthesis of CeO₂ nanostructures was performed on the surfaces of pencil graphite electrodes (PGEs). The prepared CeO₂ nanostructures were characterized using various techniques, and their surfaces were then decorated with Pd nanoparticles via electrochemical methods. Pd nanoparticles decorated-CeO₂ (Pd@CeO₂) nanostructures were characterized by Field emission scanning electron microscopy (FESEM), Energy dispersive spectroscopy (EDS), Electrochemical impedance spectroscopy (EIS) technique. The activity of Pd nanoparticle-added CeO₂ nanostructures in the electro-oxidation of ethanol was investigated, and an approximately 16-fold increase in the oxidation current density of ethanol was observed compared to CeO₂.

Keywords: CeO₂ nanostructure, Ethanol electro-oxidation, Pd nanoparticle

INTRODUCTION

With the ever-increasing need for energy and the growing environmental pollution caused by fossil fuels, the search for clean and sustainable energy has become imperative.¹ Alcohol fuel cells, which use alcohol as a source, are a good alternative energy source in terms of energy efficiency.² Among alcohol fuel cells that use inexpensive and simple fuels such as ethanol and methanol, ethanol fuel cells stand out.³ The fact that ethanol is non-toxic and can be produced from renewable sources, such as sugar fermentation or ethylene hydration, makes it an attractive fuel. In addition, ethanol is a hydrogen-rich liquid, and its energy density (8.0 kWh/kg) is higher than that of methanol (6.1 kWh/kg).^{4,5} Direct ethanol fuel cells (DECs) have been playing an increasingly important role in recent years due to their ease of use, low pollutant emissions for portable electronic devices and electric vehicles, and high energy conversion efficiency.⁶ One of the most important parameters affecting cell performance in DECs is the properties of the anode material (electrocatalyst) used.^{7,8} When selecting electrocatalysts for fuel cell applications, they must enable the complete breakdown of ethanol into carbon dioxide and water, without intermediate products such as acetate, acetic acid, or CO.^{9,10} Producing electrocatalysts with high activity and stability is crucial.¹¹ The most commonly used electrocatalyst for this purpose is the Pt electrode.^{12,13} However, the high cost of the Pt electrode, its limited availability in nature, and the ease with which the resulting CO intermediate can contaminate its surface have led to a search for new electrocatalysts.¹⁴

Recently, nanostructured transition metal oxides (M_xO_y, M=Fe, Co, Ni, Mn, etc.) have been used as alternative electrocatalysts to noble metals in alcohol fuel cells due to their multiple oxidation states and high stability.^{15–17} Among rare earth metal oxides, cerium(IV) oxide (CeO₂) is being investigated extensively due to its high oxygen-transfer capacity and catalytic properties that vary with size, shape, distribution, and surface structure. Cerium is a member of the lanthanide metals, including bastnasite, allanite, cerite, monazite, euxenite, and xenotime, and is the most abundant of the rare earth metals found in the Earth's crust.¹⁸ Cerium oxide is also called ceria. In this study, electrochemical synthesis of CeO₂ nanostructures and Pd nanoparticles was carried out on the surface of a PGE electrode. The prepared Pd@CeO₂ nanostructures were structurally and morphologically characterized using different techniques, and their activity in ethanol electro-oxidation was investigated.

MATERIALS and METHOD

Electrochemical Synthesis of CeO₂ Nanostructures

The electrolyte medium was obtained by dissolving 10 mM Ce(SO₄)₂ salt in pure water. Oxygen gas was passed through the solution. A cyclic voltamogram (CV) was recorded from the solution. Electrochemical synthesis was performed on the PGE electrode surface at a constant potential of -1.3 V for 15 minutes.

Decoration of the CeO₂ Nanostructure Surface with Pd Nanoparticles

The CeO₂ nanostructures prepared on the PGE electrode at a constant potential of -1.3 V for 15 minutes were decorated with Pd nanoparticles using electrochemical techniques. Decoration of Pd



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nanoparticles was achieved in a 0.1 M HCl solution containing 2 mM PdCl₂ at -100 mV for 7 minutes. The synthesized Pd@CeO₂ nanostructures were characterized using FESEM, EDS and EIS techniques.

Use of Pd@CeO₂ Nanostructures in Ethanol Electro-Oxidation

For the electro-oxidation of CeO₂ nanostructures prepared on a PGE electrode surface at a constant potential of -1.3 V for 15 minutes, and for CeO₂ nanostructures with added Pd nanoparticles at -100 mV for 7 minutes, a 0.5 M NaOH solution containing 1 M ethanol was used as the electrolyte. CV graphs were recorded in the potential range of -0.6 V to +0.5 V.

RESULTS

Characterization of Pd@CeO₂ Nanostructure

Morphological characterization of CeO₂ nanostructures decorated with Pd at a constant potential of -100 mV for 7 minutes was performed using the FESEM technique. The FESEM image shown in Figure 1 was recorded at different magnifications. At a magnification of 20000x, deposition on the PGE surface is clearly visible (Figure 1a). At a higher magnification (100000x), Pd nanoparticles accumulated on the surface as spherical particles (Figure 1b). Furthermore, in the EDS spectrum, in addition to peaks from the CeO₂ nanostructures, a Pd peak was observed (Figure 1c). No other elemental peaks were observed. The EDS spectrum given in Figure 1c shows that elemental-sized pure Pd@CeO₂ nanostructures can be produced using electrochemical techniques. In addition, our previous studies have supported the idea that CeO₂ nanostructures can be structurally obtained using electrochemical techniques.¹⁹

Electrochemical impedance spectroscopy (EIS) was used to investigate the superior electrochemical properties imparted by Pd decoration to the CeO₂ electrode. Nyquist plots associated with the EIS spectrum recorded in 0.5 M NaOH electrolyte containing 1 M ethanol are given in Figure 2. Two critical regions are found in the EIS spectra of Pd@CeO₂ and CeO₂ electrodes. The first region has a semi-circular appearance and provides information about the electron transfer rate at the electrode/electrolyte interface. The second region, which exhibits linear variation, includes information about the ion transport rate at the electrode. When comparing the EIS spectra of Pd@CeO₂ and CeO₂ electrodes, the semi-circular diameter of the Pd@CeO₂ electrode is smaller than that of the CeO₂ electrode. This indicates that the Pd@CeO₂ electrode has a lower electron-transfer resistance, thereby exhibiting higher electrocatalytic activity in the ethanol electro-oxidation reaction.

Ethanol electro-oxidation on Pd@CeO₂ Nanostructure

To compare the positive effects of Pd decoration on the ethanol oxidation of CeO₂, CV graphs of Pd nanoparticle-decorated and undecorated CeO₂ electrodes in 0.5 M NaOH electrolyte containing 1 M ethanol are presented in Figure 3a. CV graphs were recorded at a scan rate of 50 mV/s between -0.6 V and +0.5 V. As seen in Figure 3a, the Pd@CeO₂ electrode exhibited a specific and high-current peak towards ethanol oxidation. Examination of these graphs shows that Pd decoration increased

the current of CeO₂ by 16-fold.

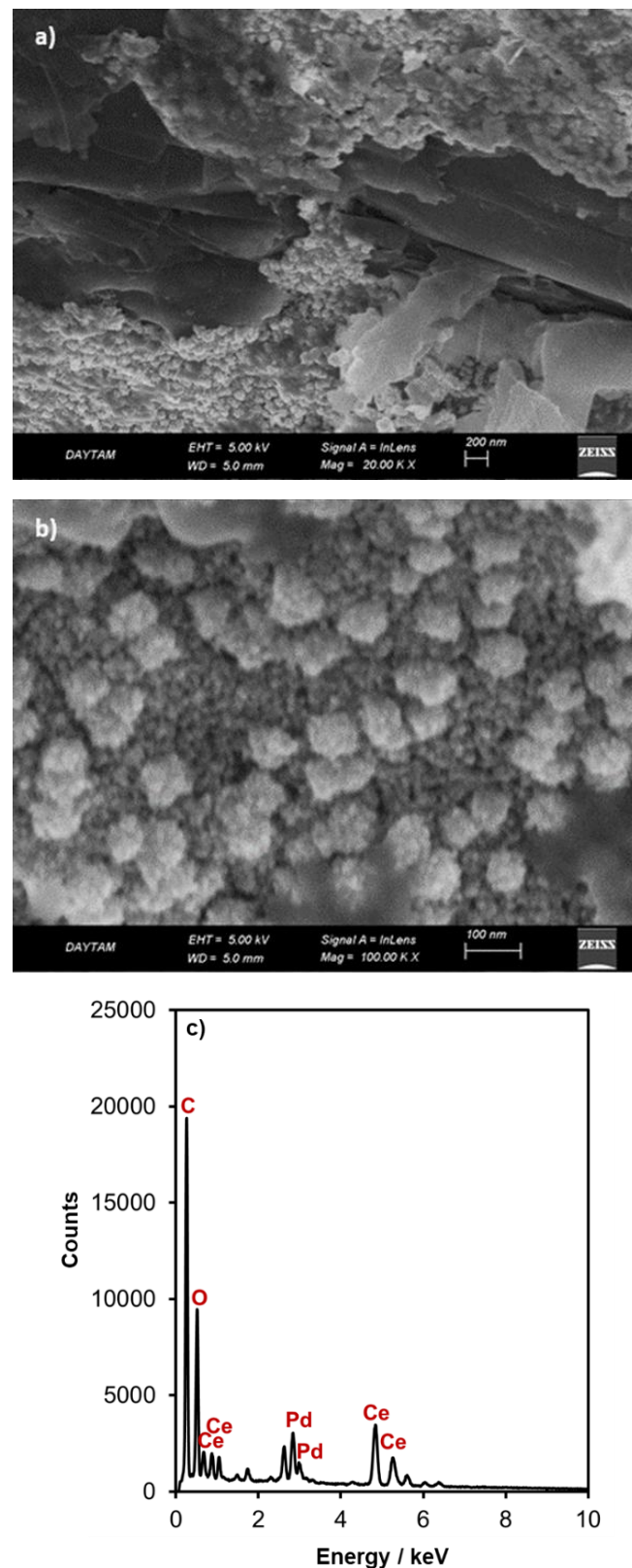


Figure 1. FESEM images (a,b) and EDS spectra (c) of Pd@CeO₂ electrode

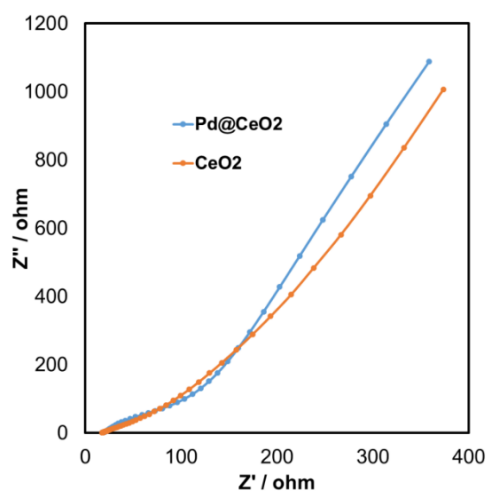


Figure 2. EIS spectrum of CeO₂ and Pd@CeO₂ electrode

Ethanol electro-oxidation on Pd@CeO₂ Nanostructure

To compare the positive effects of Pd decoration on the ethanol oxidation of CeO₂, CV graphs of Pd nanoparticle-decorated and

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To investigate the ethanol oxidation mechanism in Pd@CeO₂ nanostructures, CV graphs were recorded at different scan rates (Figure 3b). Both capacitive current and oxidation current increased with increasing scan rate. When the relationship between scan rate and current was examined (Figure 3c), a linear change with the square root of the scan rate was observed, indicating that ethanol oxidation in Pd@CeO₂ nanostructures occurs via a diffusion-controlled process.

For electrode stability testing, current variation was investigated in ethanol at a constant potential of +0.2 V (Figure 3d). Under prolonged current variations, the Pd@CeO₂ electrode exhibited a higher current density compared to CeO₂, which is a positive result of the Pd decoration.

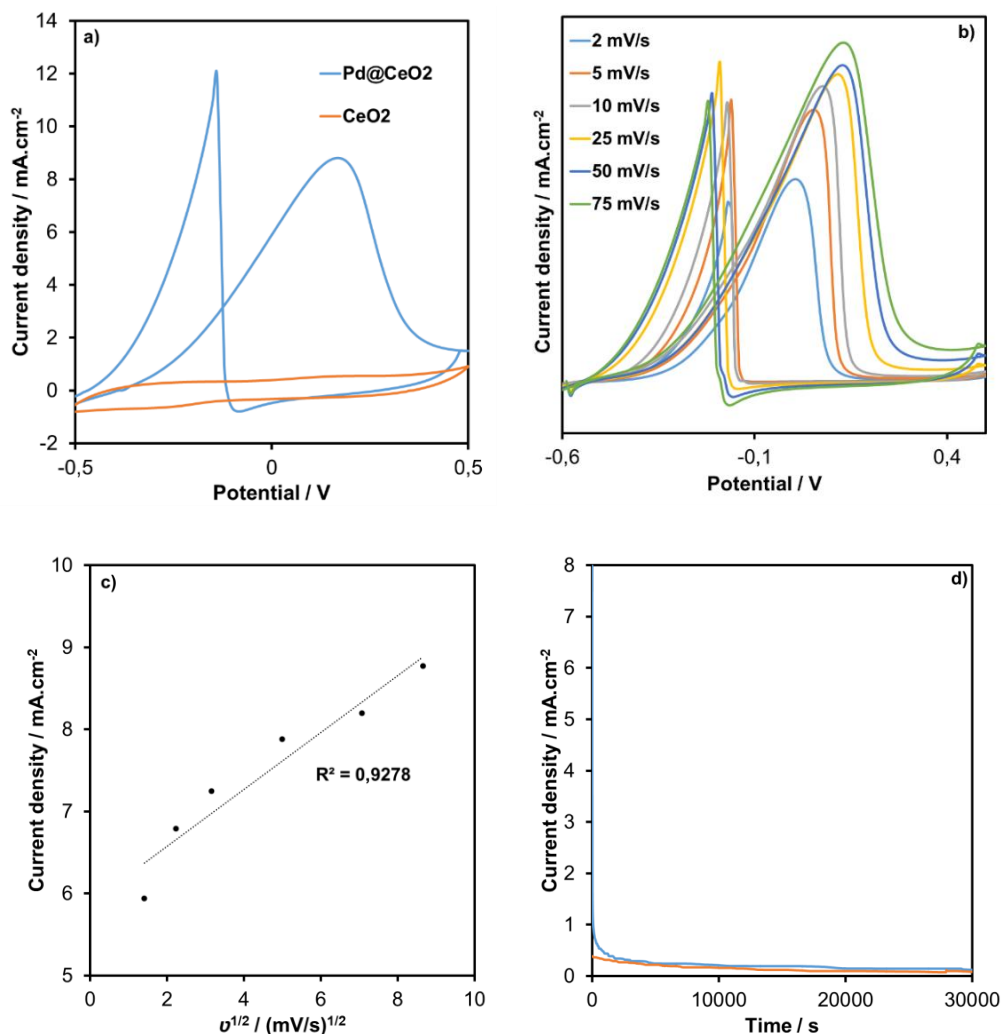


Figure 3. CVs of Pd@CeO₂ and CeO₂ electrodes in ethanol media **(a)**. Various scan rates CVs **(b)** and current density- $v^{1/2}$ graph **(c)** for Pd@CeO₂. Stable tests for ethanol electrooxidation **(d)**.

CONCLUSION

In summary, PGE electrodes modified with CeO₂ nanostructures decorated with Pd nanoparticles were successfully synthesized via electrochemical deposition. For Pd decoration, PdCl₂ salt was chosen as the Pd precursor. FESEM images showed that the PGE surface was completely coated with nanostructures. Pd, Ce, and O elements were identified in the EDS spectrum. Moreover, the EIS spectrum supported the idea that Pd nanoparticles increased the charge transfer rate of CeO₂. After Pd decoration, it was determined that the electrochemical activity of CeO₂ nanostructures increased approximately 16-fold during ethanol electrooxidation, indicating a positive contribution of Pd decoration.

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