



Coking suppression in solid oxide fuel cells operating on ethanol by applying pyridine as fuel additive



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HIGHLIGHTS

- The addition of pyridine could decrease the coke formation rates of Ni/Al₂O₃.
- The addition of pyridine could improve the operational stability of the fuel cells.
- Pyridine preferentially occupied the surface acidic sites of Ni/Al₂O₃.
- High power output of 1111 mW cm⁻² was obtained with ethanol-pyridine at 750 °C.

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ABSTRACT

In this study, pyridine was used to suppress the coke formation in solid oxide fuel cells (SOFCs) operating on liquid fuels. Pyridine can selectively occupy acidic sites of the Ni/Al₂O₃ catalyst layer and solves the problem of dehydration of ethanol in principle, resulting in a significant reduction in the coke formation rate for operating on ethanol fuel. At 600 °C, by adding 12.5 vol.% pyridine into the ethanol fuel, the coke formation rate over the Ni/Al₂O₃ catalyst is reduced by 64% while a cell power output comparable to that operating on hydrogen is still achieved based on total potential hydrogen available from ethanol. The effective reduction of carbon deposition on the catalyst layer thus protects the anode layer from carbon deposition by strongly suppressing coke formation, especially near the anode-electrolyte interface. Pyridine is adsorbed onto the acidic sites of the Ni/Al₂O₃ catalyst and the adsorbed pyridine may reduce the amount of carbonium ions formed, thereby reducing coke formation. This study suggested that the addition of pyridine could suppress the coke formation in SOFCs with Ni/Al₂O₃ catalyst layer operated on ethanol or some other similar liquid fuels.

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1. Introduction

Energy is fundamental for maintaining high quality of our life, and a sustainable supply of green energy is critical for the healthy development of our society. By considering limited resources of fossil fuels, renewable biofuels have attracted more and more attention as alternative sources of energy supply. Among them, bioethanol, which can be derived from agricultural byproducts and

biomass, has been paid special importance over the past years. On the other hand, increasing the conversion efficiency during the fuel utilization is also helpful towards a sustainable future; in this regard, fuel cells represent a superior technology for generating electric power from fuels. The combination of renewable energy materials and fuel cell technology could provide a highly efficient way to create a sustainable energy supply for the future.

As high temperature electrochemical devices, solid oxide fuel cells (SOFCs) have received worldwide attention over the past decades because of their relatively low cost, improved tolerance towards impurities, and fuel flexibility [1–4]. Ethanol as a fuel for SOFCs offers the advantages of wide availability, high energy density, and convenience in handling, transportation and storage. Low-temperature SOFCs operating on ethanol fuel may serve as an

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alternative power source for portable applications [5–7]. Nickel cermet, which are the state-of-the-art anode materials for SOFCs, exhibit excellent activity for hydrogen electrocatalytic oxidation and high electrical conductivity; however, they also catalyze the pyrolysis of hydrocarbons and oxygenated hydrocarbons. Thus, rapid deterioration in performance often occurs when these fuel cells operate on carbon-containing fuels because of significant coke formation over the nickel anode surface. To realize the operation of SOFCs on ethanol fuel, the coking problem has to be solved.

Up to now, several attempts have been conducted to reduce the coke formation over the anode of SOFC operating on ethanol fuel, such as developing high coking-tolerant nickel-free alternative copper-ceria cermet and perovskite oxide anode materials, pre-reforming fuels to hydrogen before the fuels entering the anode chamber, and internal fuel reforming using suitable catalysts [8–11]. For internal reforming, the catalyst may be positioned near the anode surface, integrated into the fuel cells in the form of a thin film coating over the anode, or impregnated into the pore wall of the anode [10,12,13]. The fuels are converted to hydrogen and CO over the thin-film catalyst layer before they reach the anode layer, thereby increasing the power output because H₂ and CO have a higher electrochemical oxidation rate than that of most carbon-containing fuels over a nickel cermet anode. Improved operational stability is also expected due to reduced coke formation over a nickel cermet anode using reforming gas (H₂ and CO) instead of hydrocarbons and oxygenated-hydrocarbons as the direct fuel and the blocking effect of the catalyst layer for the diffusion of the primary fuel to the anode layer. There are a number of literatures concerned on the development of the coking-resistant catalysts for steam reforming of ethanol reaction and a large amount of steam as high as steam to carbon ratio of 3.0 was needed to avoid the coke formation totally [14]. However, the fuel cell could not stand for such a high content of water in the fuel since reduced overall fuel efficiency and increased internal stress will be observed with such a high steam amount. As a result, the amount of steam should be minimized in the fuel cell system.

It is well known that surface acidic sites of a catalyst usually promote the cracking reaction of hydrocarbons and consequently enhance coke formation [15]. Introducing some basic element(s), such as La, Ba, Li and Mg, into the anode could effectively decrease the amount of surface acidic sites, thereby suppressing coke formation [16–18]. The basic oxides have several effects such as it neutralizes the acidic sites which would catalyze coke deposition via the carbonium ion mechanism, and catalyzes the gasification of the adsorbed carbon deposits, thus suppress the coke formation [19]. Sometimes, such foreign elements may however significantly impact the ionic transportation properties of the electrode, thus decreasing the cell power output. The addition of a basic gas to the fuel to occupy the acidic sites of the Ni-based catalysts could be a useful way to solve the problem of coke formation. The selection of the basic gas should be carefully considered and the probes for the examination of acidic sites could be excellent additives to the fuel gas to reduce the coke formation. Infrared spectroscopy (IR) and temperature-programmed desorption (TPD) has been used extensively to measure catalyst acidity and the widely used detecting probes are ammonia and pyridine.

Recently, we developed a new and facile way of reducing coke formation rate over a conventional nickel cermet anode for methane operation by simply introducing ammonia, a basic gas, as an additive to methane [20]. Ammonia preferentially occupied the surface acidic sites of both the anode and the catalyst layers to suppress methane adsorption, thus decreasing the coke formation rate. Unfortunately, NH₃ easily decomposed in the presence of a nickel catalyst at temperature as low as 600 °C [20]. Most of the ammonia likely decomposed at the temperatures when partial

oxidation or steam reforming of methane started to occur, thus reducing the efficiency of the suppression of coke formation. As a basic gas, ammonia also reacts easily with ethanol in the presence of transition metal catalysts, making the use of ammonia as an ethanol fuel additive impractical. Actually, the products for the reaction between NH₃ with ethanol at elevated temperatures are very complex, including ethylamine, diethylamine as well as the acetonitrile, which are very poisonous. Based on the thermodynamic software (HSC Chemistry ver. 5.0), the equilibrium constants of the above reactions are very large and increased with the increase in temperature (typically $\lg K > 5$ at 600 °C), suggesting the reverse reaction should be impossible to happen at above 600 °C. As a result, the combination of ethanol and ammonia are not practical.

In this study, we reported for the first time that significant improvement of coking resistance of SOFCs with conventional nickel cermet anode operating on ethanol fuel was successfully achieved by applying pyridine as a fuel additive in combination with the adoption of an anode catalyst layer, while high power output and good operational stability are obtained. It provides a novel and facile means of effectively suppressing coke formation over SOFC anodes for operation with ethanol fuel.

2. Experimental section

The fuel cell used for performance testing was in an anode substrate-supported thin-film electrolyte configuration, and an anode catalyst layer was used for improving ethanol decomposition/reforming reactivity. The anode material was a mixture of NiO + (Y₂O₃)_{0.1}(ZrO₂)_{0.9} (YSZ) with a NiO to YSZ weight ratio of 60:40, prepared by physical mixing. YSZ, Sm_{0.2}Ce_{0.8}O₂ (SDC) and Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} (BSCF)/Sm_{0.5}Sr_{0.5}CoO_{3- δ} (SSC) composite was used as the materials of electrolyte, buffer layer and cathode, respectively. Two types of catalysts were used: a Ni/Al₂O₃ catalyst which was composed of 15 wt.% nickel with the balance being Al₂O₃, and a Li and La co-modified Ni/Al₂O₃ catalyst which was composed of 15 wt.% nickel, 1 wt.% Li₂O, 5 wt.% La₂O₃ with the balance being Al₂O₃. The catalysts were synthesized by a glycine nitrite process (GNP), which has been described in detail elsewhere [20], whereas the BSCF, SDC and SSC cathode materials were synthesized by an EDTA-citrate complexing sol-gel process [21].

Half cells of Ni-YSZ anode substrate supported thin film YSZ electrolyte with SDC buffer layer were prepared by tape-casting for the anode-YSZ dual layers and screen-printing for the buffer layer, in combination with corresponding sintering processes [20]. A mixture of BSCF/SSC + SDC (in a 7:3 weight ratio) was used for the cathode, which was screen-printed onto the central surface of the electrolyte and then fired at 1000 °C in the air for 2 h. The effective geometric surface area of the cathode was 0.48 cm², which was used for the calculation of cell power output. The anode surface was coated with a thin catalyst layer to enhance the ethanol reforming reaction and the catalyst layer was further sintered at 750 °C for 1 h. The current collector in the stability test was created by using a stick to draw a mesh-like morphological structure of silver paste onto the cathode surface.

Coke formation over the catalysts was investigated by first treating the catalysts in an atmosphere composed of 37.5 vol.% ethanol+62.5 vol.% helium or 37.5 vol.% ethanol+12.5 vol.% pyridine+50 vol.% helium for 30 min, then the catalysts were subjected to an oxygen temperature-programmed oxidization (O₂-TPO) analysis. The laser Raman spectra of the catalysts were obtained after treating the catalysts in ethanol-containing atmospheres for 30 min using an HR800 UV Raman microspectrometer (JOBIN YVON, France) with the green line of an argon laser ($\lambda = 514.53$ nm) as the excitation source. The morphologies of the

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