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Degradation behaviors of SOFC due to chemical interaction between Ni-YSZ anode and trace gaseous impurities in coal syngas

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ABSTRACT

The influence of the selected trace species of S, Cl, and Si contained in post-CCS (Carbon Capture and Storage) hydrogen-enriched coal syngas in the EAGLE integrated gasification combined cycle with carbon capture and storage (IGCC/CCS) pilot plant on the performance of solid oxide fuel cell (SOFC) with cermet anode of NiO and yttria-stabilized zirconia (YSZ) was examined. We conducted power generation tests using an electrolyte-support single button-shaped cell fueled by simulated post-CCS syngas with H_2S, HCl, and tetraethylorthosilicate (TEOS) to determine whether the performance of the SOFC anode was affected by the trace impurities. We confirmed that injections of trace levels of H_2S ranging from 1 to 10 ppm always resulted in a modest but abrupt performance drop soon after injection, the magnitude of which depended on H_2S concentration as well as current densities. Long-term exposure tests fueled by simulated syngas with H_2S or HCl did not reveal any appreciable acceleration in performance degradation in the presence of impurities, although there was a small amount of sintering of component particles in the diffusion layer. Injection of TEOS, a chemical substance representing Si vapor source, resulted in performance degradation with an increase in ohmic and polarization resistances. Deposition of Si species occurred on the surface and in the boundary region of the active and diffusion layers of the anode. Plausible diffusion and deposition mechanisms of trace gaseous Si species around the layered Ni-YSZ anode, possibly caused by thermal polymerization of TEOS and generation of SiO due to hydrogen-induced SiO_2 reduction, are presented.

1. Introduction

As a consequence of vulnerability resulting from the oil crisis in the 1970s and the subsequent debates on reassessment of the national primary energy mix to lessen extreme dependence on foreign oil resources, Japan has made serious efforts to increase diversification of its overseas energy supply sources. In March 2011, the Great East Japan Earthquake and resulting tsunami severely damaged the Fukushima Daiichi nuclear power plant. Consequently, Japan has been obliged to revise its energy policy to reduce dependence on nuclear power. Under these circumstances, coal is recognized as a crucial base-load energy resource because of its economy, abundance, and minimal association with political instability [1–4]. Fig. 1 shows the process diagrams of conventional and anticipated coal-based power plants in Japan. About 30% of domestic electricity is supplied by conventional pulverized coal (PC) fired power generation facilities and the state-of-the-art PC power plant, Isogo power plant #2, has an efficiency of 40% [5]. Efficiency improvements to the conventional process must be promoted, and more advanced power generation processes for achievement of efficiency gains and low carbon emissions from coal-based power generation explored.

Since 1983, the New Energy and Industrial Technology Development Organization (NEDO) has undertaken a national project for the research and development of advanced power generation processes, including the integrated gasification combined cycle (IGCC) [6]. The IGCC uses a high-pressure air-blown coal gasifier to produce syngas. The syngas is processed to remove impurities such as acidic gases (e.g., hydrogen sulfide, hydrogen chloride), mercury, alkali and alkaline earth metals, and other particulates [7,8] and then used to drive a gas turbine, which produces electricity. The high temperature produced by the gas turbine is recovered to generate additional steam that drives a steam turbine to produce additional electricity. The IGCC has the potential to improve the efficiency of coal-based power generation with increased flexibility regarding coal feedstock. After a feasibility study and preliminary investigations, NEDO eventually started the first large-scale (250 MW) air-blown IGCC demonstration project in 2007 under the operation of Clean Coal Power R&D Co., Ltd. in Nakoso, Fukushima. They confirmed targeted performance, reliability, and wide applicability of coal feedstocks through long-term operation tests (cumulative operation time: 18,788 h) [9]. The air-blown IGCC plant has been operated commercially by Joban Joint Power Co. Ltd. since 2012 [10].

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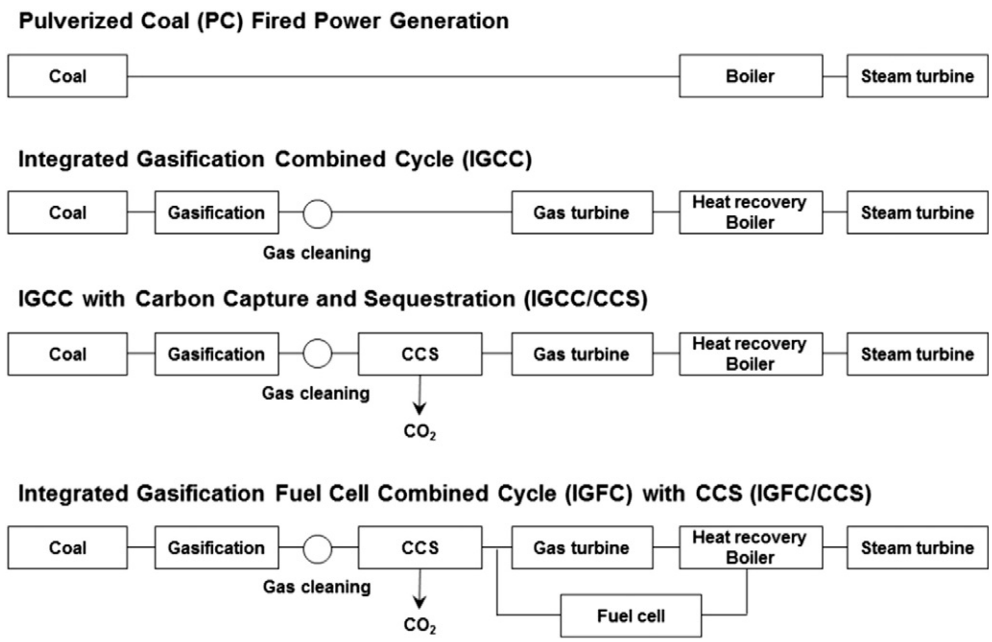

Fig. 1. Process diagrams of conventional and anticipated coal-based power plants in Japan.

In order to realize more efficient coal-based power generation as well as multi-purpose coal syngas production with reduced carbon emissions, NEDO launched another demonstration project (the EAGLE project) on an advanced coal gasification process in 1995 and then started operation of a pilot-scale gasification plant with a capacity of 150 t-coal/day in 2002 [11]. In EAGLE step 1 (2002–2006), the project developed the oxygen-blown entrained flow gasifier with single-chamber two-staged spiral flows and a wet gas cleanup system to achieve stable and efficient production of clean syngas from coals. To realize further reduction of carbon emissions from IGCC, and the coupling of fuel cells to coal gasification, EAGLE step 2 (2007–2009) investigated additional subjects in the processes of CO_2 removal and recovery from coal syngas (IGCC/CCS as shown in Fig.1), the gasification behaviors of coals with different ash melting temperatures, and the behavior of trace elements in the EAGLE gasification plant. Based on the experiences of and findings obtained in the eight year EAGLE demonstration project, a new national project was launched in 2015 in Japan [12]. This project, called the Osaki Cool Gen Project, uses a scaled-up version of the EAGLE gasifier (1100 t-coal/day) and aims to establish commercial-scale advanced IGCC/CCS to offer efficiency as well as zero carbon emissions in coal-based power generation. In addition, in the second half of the project, the coupling of a high-temperature and fuel-flexible solid oxide fuel cell (SOFC) into the IGCC/CCS plant is scheduled. This coupling is often referred to as the integrated gasification fuel cell combined cycle (IGFC). In the Osaki Cool Gen project, the SOFC will be attached in the downstream of the water-gas shift reactor and CO_2 capture unit so that the resultant H_2-enriched (after CO_2 removal) fuel gas will be supplied to the SOFC.

SOFC is an energy conversion device that uses solid oxide electrolytes to transport negative ionized oxygen from the cathode to the anode and efficiently produce electricity, through the electrochemical oxidation of fuels over the anode at high temperatures ranging from 873 to 1273 K [13–15]. Due to the very high temperatures, SOFC can be operated with direct fueling of light hydrocarbons (e.g., CH_4) with internal or dry reforming within the anode [16–18]. In principle, SOFC can also accept the reformates (mixtures of H_2, CO, CH_4, and steam) derived from externally reformed heavier hydrocarbons, and the syngas derived from the coal or biomass gasification as a fuel. So far, a number of studies [19] have been conducted to examine the performance of SOFC fueled by natural gas or reformates from externally reformed natural gas because such fuel gases are readily available.

There are some technical concerns associated with the IGFC/CCS process, regarding the occurrence of performance degradation of the SOFC anode caused by chemical interaction between the anode material and trace impurities contained in the coal-derived syngas. Coal is a complex heterogeneous mixture of organic and inorganic constituents with allogenic or authigenic origin. Typical syngas obtained from high temperature coal gasification is predominantly composed of H_2 and CO but also contains trace levels of various impurities such as condensable hydrocarbons (tar), soot, acidic and halide compounds, and heavy metal vapors. In practice, according to reports [10–12,20,21], the produced syngas is subjected to subsequent wet gas cleaning and the level of impurities in the syngas is eventually lowered below the maximum acceptable ranges for avoiding corrosion of gas turbine blades in the IGCC system. The typical required concentrations for acidic (H_2S) and halide compounds (HCl, HF) are less than 1 ppm. However, in the case of SOFC fueled by coal-derived syngas in the IGFC system, the degradation of SOFC materials would occur even with ppm or sub-ppm level contamination of poisonous gas and vapor in the syngas, as has already been shown [22–32]. The fates of heavy metal vapors and inorganic compounds are also an important issue to be considered. Trace impurities in coal particles are volatilized under the reducing conditions in a high temperature coal gasifier and are subsequently partitioned between ash and gas phase fractions depending on the volatility of the trace impurities. Taking the volatility of the selected elements into account, Trembly et al. examined the fates of the trace impurities in coal based on the thermodynamic equilibrium calculation [33]. They deduced that volatile species such as Sb, As, Cd, Hg, Pb, P, and Se may form in vapor phase under the warm gas cleanup conditions and Sb, As, and P vapor phase species will have the potential to form secondary Ni phases in the SOFC anode, leading to serious performance loss at the anode. However, the behavior of such trace elements in the whole IGCC or IGCC/CCS process is still unclear because conventional analytical methods are not fully established for the sampling, identification, and quantification of a wide variety of trace species. The EAGLE project applied the official wet absorption method to collect trace species in real syngas and eventually found that sub-ppm concentrations of gaseous S, Cl, and Si remained in the post-CCS syngas, which is the resultant