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Iso-octane internal reforming in a solid oxide cell reactor

A. Al-Musa [a], N. Kaklidis [b], M. Al-Saleh [a], A. Al-Zahrani [a], V. Kyriakou [c,d,*], G.E. Marnellos [b,d,e]

[a] National Center for Combustion and Plasma Technologies, Water & Energy Research Institute, King Abdulaziz City for Science & Technology, 11442, Riyadh, Saudi Arabia
[b] Department of Mechanical Engineering, University of Western Macedonia, 50100 Kozani, Greece
[c] Department of Chemical Engineering, Aristotle University of Thessaloniki, Building E13, 54124, Greece
[d] Chemical Process & Energy Resources Institute, Centre for Research & Technology Hellas, 57001 Thermi, Thessaloniki, Greece
[e] Department of Environmental Engineering, University of Western Macedonia, 50100 Kozani, Greece

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ABSTRACT

This study reports on the feasibility of internal iso-octane steam reforming process in an YSZ solid oxide fuel cell reactor by employing Cu/CeO_2 as catalyst/anodic electrode. The Cu/CeO_2 anode is evaluated for its both catalytic and electro-catalytic performance. In all cases, i-C_8H_{18} was successfully reformed by H_2O to syngas. In addition, appreciable amounts of CO_2 and CH_4 were also produced. The distribution of products was also influenced by i-C_8H_{18} thermal pyrolysis and catalytic decomposition processes leading mainly to olefins formation. At closed-circuit operation, and by applying anodic overpotentials, mainly H_2 and CO were electro-oxidized to H_2O and CO_2, while at cathodic polarization conditions the co-electrolysis of H_2O and CO_2 to H_2 and CO was taking place, affecting the equilibrium reactions at the anodic chamber. During fuel cell operation, the electrochemical performance increased with cell temperature and i-C_8H_{18}/H_2O feed ratio. The AC impedance spectroscopy analysis showed contributions both from charge and mass transfer processes, with the latter to dominate the overall cell performance.

1. Introduction

The increasing energy demands are still mainly compensated by fossil fuels employing thermodynamic limited conventional heat cycle configurations [1]. In recent years great advances have been accomplished in Renewable Energy Sources (RES) technologies. However, the high cost and complexity for RES adaptation and exploitation have made them prohibitive to be implemented currently in stationary power plants. This “business as usual” scenario is leading to natural sources depletion and significant environmental implications, which is in contrast with the strategies for a sustainable future imposed by international organizations.

Fuel cells are considered as a promising energy conversion technology, capable of satisfying the needs of high efficiency and low environmental footprint [1]. Although, H_2 is the ideal fuel for fuel cells, several obstacles related to its limited availability, the absence of relevant infrastructure and the difficulties associated with its storage and transport retard the market roll out of fuel cells [2]. In the meantime, the use of conventional fuels with established infrastructure, like gasoline, could be an alternative way to accelerate the commercialization of fuel cells. SOFCs, due to their high operating temperature can be potentially operated directly on conventional hydrocarbon fuels [3–9].

The key-issue of liquid fuel-fed SOFCs development is the selection of the anodic composite materials. An electro-catalyst for this application should mainly exhibit a) high catalytic activity for hydrocarbon oxidation and reforming, b) adequate electron conductivity and c) high tolerance to carbon deposition. The Ni-based anodes are currently the state of the art materials for SOFCs [2–6,8–13]. Nickel electrodes are fulfilling the first condition, but it has been proved that they are carbon sensitive at low C/H_2O ratios [14]. Furthermore, Ni in these cermets is oxidized easily to NiO, due to its poor redox properties suffering an important decrease in electronic conductivity [15–18]. Hence, the development of electro-catalytic active and conductive anodic materials, tolerant toward carbon poisoning, is of crucial importance [3,4].

Among others, Cu-based cermets have been proved as the most promising candidates for direct hydrocarbon SOFCs, because they perfectly fulfill all the aforementioned prerequisites. In a recent study it was demonstrated that their performance is improved when a thin layer of carbonaceous compounds is deposited on their surface after paraffin fuel treatment [3]. In addition, Gorte et al. also demonstrated that the $Cu\text{-}CeO_2$ cermets show excellent stability in their relevant direct hydrocarbon SOFC works [6,7,15,19].

In the present study, typical fuel cell measurements and AC impedance spectroscopy studies are combined to investigate the performance of an iso-octane internal steam reforming solid oxide reactor cell of the type $Cu\text{-}CeO_2/YSZ/Pt$. Iso-octane is used as fuel, because it is a common surrogate for gasoline and has lower tendency for cracking than other heavier hydrocarbons [20]. Furthermore, the catalytic and electro-

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[*] Corresponding author at: Department of Chemical Engineering, Aristotle University of Thessaloniki, Building E13, 54124, Greece. Tel.: +30 2310 996145.
E-mail address: kyriakou@cperi.certh.gr (V. Kyriakou).

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catalytic behavior of Cu-CeO_2 anodic composite is also evaluated under open- and closed-circuit modes of operation.

2. Experimental

The apparatus employed for the electrochemical measurements during iso-octane internal reforming, has been described in detail in previous communications [5,12]. The employed cell is consisted of an 8 mol% Y_2O_3-stabilized ZrO_2 (YSZ) solid electrolyte tube (15 cm long, 16 mm ID, 18 mm OD, 1.2 mm thickness, supplied by CERECO) closed at its one end and three electrodes applied on its both sides. On the outer surface of the closed-end, two porous Pt films were deposited and served as counter and reference electrodes similarly to our previous works [5,11,12], while on the inside bottom surface a 70 wt.%Cu–30 wt.%CeO_2 mixed oxide composite was employed as anode. The Cu/CeO_2 working electrode was prepared from cerium (IV) oxide (99.9%, Alfa Aesar) and copper powders (99%, Alfa Aesar), respectively [5,12]. Appropriate quantities of both chemicals were diluted in 20 ml of ethyl glycol, fired at 200 °C and stirred at 400 rpm until half of the volume was evaporated. The resulted viscous suspension was deposited on the inside bottom of the YSZ tube by painting. The tube was then heated up to 900 °C, and calcined for 4 h. The Cu/CeO_2 electrode thus formed had a superficial surface area of 1.7 cm^2 and its morphology, structure and composition was analyzed employing various characterization techniques, using a previously removed from the YSZ surface Cu/CeO_2 electrode film [5,12]. The surface area was measured using the BET method, and was found equal to 2 m^2/g. The elemental mapping revealed that the microstructure is non-uniform, with the CeO_2 and Cu phases randomly distributed. For XRD analysis, the Cu/CeO_2 catalyst was first deposited as anodic electrode and it was treated with pure H_2 under open circuit and anodic polarization conditions ($\eta = 3000$ mV) at 850 °C. Then, the electrode was removed from the solid electrolyte surface and subjected to XRD analysis, where Cu, CeO_2 and Cu_2O phases were observed in the corresponding diffraction spectra [5]. The metallic Pt counter and reference electrodes were prepared from an organometallic paste (Metalor) after calcination in static air at 900 °C for 4 h. The heating and cooling rates in all steps were kept at 4 °C/min.

The experimental apparatus [5,12] is comprised of a liquid reactants feed unit equipped with the necessary heated saturators, the solid electrolyte cell reactor and the gas analysis system. The measurements were carried out in the temperature range of 750–850 °C under atmospheric pressure and a total flowrate of 75 cm^3/min. Various mixtures of iso-octane and water vapors were fed into the cell reactor by bubbling pure He (Air Liquide) through two different vessels containing i-C_8H_{18} (99.5% purity, Riedel-de Haen) and twice-distilled water. Both vessels were insulated and heated at specific temperatures in order to obtain the desired amounts of iso-octane and water vapors, while the remaining flow lines up to cell reactor inlet provisions and the GC were heated at 100 °C. The reactant and effluent composition was monitored with a SHIMADJU 14B gas chromatograph (GC) equipped with thermal conductivity (TCD) and flame ionization (FID) detectors as well as with a Molecular Sieve 13X and a Porapack QS column for gas separation. The carbon and water contents were always calculated using the carbon, hydrogen and oxygen mass balances.

The cell voltage and developed electrical current were controlled and monitored by means of an AMEL model 2053 Potentiostat-Galvanostat and two differential voltmeters (Digital Multimeter DT9205A). For the fuel cell measurements, the cell characteristics were acquired employing a resistance box 1051 by Time Electronics. AC electrochemical impedance spectra were acquired under open circuit conditions in the frequency range from 0.01 Hz to 1 MHz, with an amplitude of 30 mV RMS, using the IVIUM technologies electrochemical workstation and the corresponding software (IVIUMSOFT) for data processing. Prior to each experiment the anodic electrode was pretreated with pure H_2 at 850 °C for 3 h.

3. Results and discussion

3.1. Open-circuit studies

Open-circuit experiments were firstly carried out to demonstrate the catalytic activity of Cu-CeO_2 anodic electrode for iso-octane steam reforming (ISR). Fig. 1 shows the effect of temperature on the products' formation rate, open-circuit voltage (OCV) and reactants conversions. The inlet partial pressures of iso-octane and steam was 1.5 and 12 kPa, respectively, corresponding to a H_2O/C feed ratio equal to unity. The reactor cell effluent stream consisted mainly from H_2, CO, CH_4 and CO_2, while minor quantities of C_{2s} (C_2H_4, C_2H_6), and C_{3+} olefins (C_3H_6, C_4H_8) were also detected. Concerning the conversions of reactants, it seems that they both increase with cell temperature. However, iso-octane conversion is higher and its increase is more intense compared to H_2O consumption rate. The main reason is that H_2O is also a product of the parallel running reverse water gas shift (1) reaction, which is favored at elevated temperatures:

$$CO_2 + H_2 \leftarrow\rightarrow CO + H_2O \tag{1}$$

In addition, the catalytic decomposition and thermal pyrolysis of iso-octane could also explain the observed differences in reactants conversions. The latter is confirmed by the formation of C_2–C_4 olefins which are derived as carbonaceous fragments via the scission reactions of iso-octane [21]. Saunders and Kendall observed a similar product distribution over Ni/YSZ electrodes which was assigned to the simultaneous polymerization and decomposition processes of produced olefins [17].

The observed H_2/CO ratio is equal to 2.8 at 750 °C, a value higher than the stoichiometric ratio (2.1) expected for ISR, and decreases with temperature becoming equal to 2 at 850 °C. At the same time, the CO/CO_2 ratio and methane production rate are also increasing with temperature. The above results clearly reveal the importance of reverse water gas shift (RWGS) reaction at these operating conditions. A similar H_2/CO ratio equaled to 2.57 was observed in the work of Flores-Marin and Su [22], who proposed that the produced CO was consumed by one or more parallel reaction pathways carried out in the reactor.

Fig. 2 depicts the dependence of the formation rate of various products, reactants' conversion and OCV on the iso-octane (Fig. 2a) and H_2O (Fig. 2b) inlet concentration. The partial pressures were ranged from 0.5–3 kPa for iso-octane under a constant $P_{H2O} = 12$ kPa (Fig. 2a) and from 3 to 24 kPa for H_2O at $P_{i\text{-}C8H18} = 1.5$ kPa (Fig. 2b), respectively. The operation temperature was kept constant at 850 °C and the total flowrate was remained always equal to 75 cm^3/min. The observed

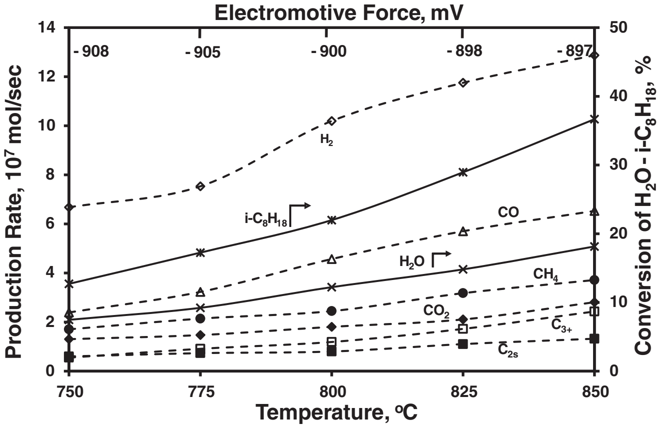

Fig. 1. Dependence of products' formation rates, i-C_8H_{18} and H_2O conversions and developed OCV on cell temperature at open circuit conditions. $P_{i\text{-}C8H18} = 1.5$ kPa, $P_{H2O} = 12$ kPa, $F_T = 75$ cm^3/min.