



Research paper

Cogeneration of ethylene and energy in protonic fuel cell with an efficient and stable anode anchored with *in-situ* exsolved functional metal nanoparticles



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ABSTRACT

In situ exsolution of Co nanoparticles on perovskite framework has been successfully synthesized by firing the porous precursor SrMo_{0.8}Co_{0.1}Fe_{0.1}O_{3-δ} (SMCFO) in reducing flow at 850 °C. A structure transformation (from mixed to pure cubic phase) and the growth of Co nanoparticles are observed in H₂ atmosphere. This leads to an increase in the oxygen vacancy content, which is beneficial to the electrical conduction and catalytic activity towards the oxidations of H₂ and C₂H₆. Moreover, this material exhibits good redox reversibility under the condition of multiple reduction and re-oxidation cycles, as confirmed by the thermogravimetric analysis (TGA) measurements. A protonic fuel cell (PFC) built with this newly developed material shows a comparable electrocatalytic activity in both C₂H₆ and H₂ atmospheres while a considerably high power density of 377 mW cm⁻² is achieved in H₂ and 268 mW cm⁻² in C₂H₆ at 750 °C. In addition, C₂H₄ yield in the cell with Co-SMCFO as anode is considerably improved (11.9%–37.8% at 650–750 °C) with respect to the widely used chromium oxide. The good electrochemical performance, the improved C₂H₆ partial dehydrogenation ability and the negligible carbon formation in the Co-SMCFO anode are the strong indications that the SMCFO is a promising catalyst for the cogeneration of C₂H₄ and electricity, and can also be potentially utilized in the PFC directly fueled with hydrocarbon.

1. Introduction

As one of the key reactions in the chemical industry, C₂H₆ dehydrogenation to C₂H₄ has been extensively studied in the past few decades due to the ever increasing demand for C₂H₄, a major intermediate for the production of polymers and petrochemicals [1,2]. Currently, the most widely employed technologies for C₂H₆ dehydrogenation include 1) energy-intensive non-catalytic steam cracking at high temperature and 2) catalytic oxidative C₂H₆ dehydrogenation. In comparison with the steam cracking, the oxidative dehydrogenation [a combination of endothermic reaction (C₂H₆ dehydrogenation: C₂H₆ → C₂H₄ + H₂) and exothermic reaction (H₂ oxidation: H₂ + 0.5 O₂ → H₂O)] shows greater potential to lower the energy requirement and consequently improve the C₂H₄ yield [3]. However, the presence of oxygen sources significantly consumes the produced H₂ and causes undesirable deep oxidation of C₂H₆ and/or C₂H₄ to CO₂ [4]. Therefore, developing alternative and more direct routes to dehydrogenate C₂H₆ to C₂H₄ is of particular interest. In this regard, protonic fuel cell (PFC) has emerged as a promising pathway to the solution of solving the problem [5,6]. In

a typical PFC utilized for cogenerating C₂H₄ and electricity from C₂H₆ oxidative dehydrogenation, H₂ is selectively removed when the protons generated from the oxidation of H₂ at anode pass through the protonic electrolyte and react with oxygen ions to form water at cathode. Moreover, since both C₂H₄ and C₂H₆ are prevented from contacting the oxygen sources, the CO₂ emission resulted from deep oxidation can be avoided. Nonetheless, the minor oxide ion conductivity in the protonic electrolyte can significantly resist the carbon deposition at elevated temperatures [1,5].

Although conventional Ni-based materials show high catalytic activity towards fuel oxidation, they can be easily deactivated during cell operation due to their sensitivity to carbon formation as a result of incomplete hydrocarbon oxidation [7,8]. However, when perovskite is utilized as supporting backbone, the incorporated B-site cation in the perovskite lattice can be partially *in situ* exsolved as functional metal nanoparticle under reducing flow, which can not only serve as co-catalyst for certain reactions, but also improve the electronic conductivity of the parent perovskite [9–11]. More importantly, this exsolving process is able to grow much finer and more evenly distributed

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nanoparticles without agglomeration and carbon formation as compared to the deposited analogues [9]. Various perovskite oxides with *in situ* exsolved metal/bimetal nanoparticles, such as Ni-(La)Sr(Ni)TiO₃ [9], Ni-Sr₂FeMo(Ni)O₆ [12], CoFe-La(Sr)(Co)FeO₃ [13] and CoFe-(Pr)Sr₃[Fe(Nb)]₂O₇ [14], have been investigated as potential anodes for solid oxide fuel cell (SOFC) using hydrocarbon gases. These anode materials show excellent catalytic activity and improved coking resistance towards hydrocarbon oxidation. One of the alternatives is the family of MMoO₃ (M = Sr, Ba, Ca) perovskites [15,16], especially the cubic SrMoO₃; they have been demonstrated the high electrical conductivity (10⁴ S cm⁻¹) at room temperature and high catalytic activity for oxidative dehydrogenation due to the presence of redox couple of Mo⁶⁺/Mo⁴⁺ [16]. Furthermore, doping with trivalent elements (Co, Fe, Cr) of stoichiometric amounts at the Mo-sites potentially enhances the mixed ionic and electronic conductivity, as identified by the group of Martínez-Coronado [17–19]. Co is an excellent electrochemical catalyst with similar catalytic properties as Ni and has less tendency towards carbon formation, thus Co has been widely studied as an anode material in SOFC [20,21]. It has also been reported that group VIII metals are capable of catalyzing C₂H₆ dehydrogenation with an activity sequence of Co > Ni > Fe [22]. Its good catalytic activity and high selectivity for C₂H₄ make Co the most attractive-candidate for this reaction [23].

In this work, catalytically active Co metallic nanoparticles were successfully exsolved and evenly distributed on the porous cubic SrMo_{0.8}Co_{0.1}Fe_{0.1}O_{3-δ} (Co-SMCFO) framework to improve the C₂H₆ dehydrogenation activity and electrochemical performance of the PFC by reducing SMCFO in 5% H₂/N₂ flow at 850 °C. This material thus fabricated was used as anode in a BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ} (BCZY) electrolyte-supported PFC. We systematically investigated the newly developed material in terms of its redox stability, the phase transformation, electrochemical performance, and C₂H₆ dehydrogenation activity towards C₂H₄ formation as well as the coking resistance. The mechanism credited for the good electrochemical performance and the high activity of C₂H₆ oxidative dehydrogenation towards C₂H₄ was also explored.

2. Experimental

2.1. Preparation and characterization of materials

Stoichiometric amounts of Sr(NO₃)₂, (NH₄)₆Mo₇O₂₄·4H₂O, Co(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O were dissolved in EDTA-NH₃H₂O solution under continuous heating and stirring, citric acid was then added. The molar ratio of EDTA acid: citric acid: total metal ions was controlled to be around 1: 1.5: 1. Subsequently, NH₃H₂O was added to adjust the pH value to be around 8. The solution was stirred and heated on a hot plate at 80 °C until the formation of organic resins containing the homogeneously distributed cations because of the slow evaporation of the solvent. The synthesized gel was decomposed at 300 °C for 4 h to remove the organic components and the nitrates. The precursor powders were then fired at 1100 °C for 10 h in air to obtain the raw materials which were subjected to further heating in a tubular furnace at 850 °C for additional 10 h in a reducing gas flow (~10⁻¹⁹ atm of P_{O₂}) to eventually form the *in situ* exsolved Co-SMCFO.

Thermogravimetric analyses (TA SDT Q600) were performed from 20 to 1000 °C at a heating/cooling rate of 10 °C min⁻¹ in air or 5% H₂/N₂ to characterize the thermophysical properties. The crystalline structure of all the synthesized powders was identified by X-ray diffraction (XRD) with Rigaku Rotaflex Cu Kα radiation (40 kV, 44 mA) and the raw data were analyzed with JADE version 6.5. Microstructures were determined with a high-resolution Zeiss Sigma FE-SEM equipped with an EDX detector and an EBSD detector. X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra) was used to investigate the surface chemistry of the SMCFO and Co-SMCFO powders with the CasaXPS software, the adventitious carbon (C 1s) at the binding energy (BE) of 284.6 eV was used as the reference. Nicolet Almega XR Dispersive

Raman Microscope with 532 nm laser and X50 objective was used to determine the level of coke deposition on the Co-SMCFO after the stability test.

2.2. Cell fabrication and testing

The single cells investigated in this work were BCZY electrolyte supported. The anode material slurry was prepared by combining Co-SMCFO or NiO and BCZY (weight ratio of 1:1) with a glue containing 1-butanol, benzyl butyl phthalate (BBP), ethyl cellulose and alpha-terpineol. The weight ratio of catalyst and glue was 1.7:1. A cathode electrode comprised of LSCF and BCZY was prepared with the same method as that for the anode material slurry. Both the anode and cathode material slurries were screen-printed onto the corresponding surfaces of the BCZY disc to form a membrane electrode assembly (MEA). The MEA was sintered at 1000 °C for 2 h in air. Gold paste was painted onto the surfaces of both anode and cathode to form current collectors. The PFC was built by fixing the MEA between coaxial pairs of alumina tubes with a sealant, which was fastened in a vertical tubular furnace (Thermolyne F79300). Dry C₂H₆ was fed to the PFC with a flow rate of 100 ml min⁻¹ via the anode tube located on the bottom, while the cathode, placed on the top, was exposed to air.

Electrochemical measurements were performed after the furnace reached a stable temperature. The electrochemical performances of the cell were measured by employing a four-probe method with Au wires as the leads. The electrochemical measurements were conducted with a Solartron 1255 frequency response analyzer and a Solartron 1286 electrochemical interface instrument. The temperature of a single cell was slowly increased to 850 °C and a 5% H₂/N₂ reducing gas flow was continuously pumped into the anode compartment. The temperature was held for 2 h to complete the further reduction of the anode material, the temperature was then decreased to 750 °C and 700 °C for electrochemical measurements. Stability test in C₂H₆ atmosphere was performed under a constant current load at 700 °C. The outlet gases from the anode compartment were analyzed using a Hewlett-Packard model HP5890 GC equipped with a packed bed column (Porapak QS) operated at 80 °C with a thermal conductivity detector and a flame ionization detector.

3. Results and discussion

The precursor powders of SMCFO were synthesized using a modified sol-gel method, as described elsewhere [24]. The corresponding X-ray diffraction (XRD) pattern of the SMCFO powders was obtained by Rigaku diffractometer (Cu Kα radiation, 40 kV, 44 mA) after firing in air at 1100 °C for 10 h (Fig. 1a). Clearly, the as-synthesized powders are a mixture of cubic (†) and tetragonal phases (Δ), where the standard SrCoO_{2.29} (PDF #39-1083) shows a cubic structure with lattice constants of a = b = c = 3.912 Å, and the standard SrMoO₄ possesses a tetragonal phase [space group: I41/a(88)] with lattice parameters of a = b = 5.394 Å and c = 12.020 Å. However, it is found that SMCFO shows a pure single phase (PDF # 24-1224) without any impurities after firing in a reducing atmosphere (Fig. 1b). This agrees well with the standard structure of SrMoO₃ in the space group of pm-3 m (221) with the lattice constants of a = b = c = 3.974 Å, which indicates the successful preparation of SMCFO under reducing condition. The elimination of the SrCoO_{2.29} is due to the Co exsolution and the annihilation of oxygen vacancies. Generally, the introduction of the cations with smaller ionic radius like Co³⁺ (0.615 Å) and high spin Fe³⁺ (0.645 Å) at B-site of Mo³⁺ (0.65 Å) increases the 2θ and θ angles and consequently, decreases the unit cell parameters [17,25,26]. A closer examination of the enlarged zone at the phase of (100) reveals that the diffraction peak of SMCFO after firing in reducing flow shifted to a larger angle as expected with corresponding diffraction angle changing from 22.38° to 22.55° (Fig. 1c). It is also worth mentioning that the substitution of B-sites by lower valence cations of Co and Fe causes the

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