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Application of $BaTiO_3$ as anode materials for H_2S-containing CH_4 fueled solid oxide fuel cells

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ABSTRACT

Undoped $BaTiO_3$ perovskite oxide is more effective than $SrTiO_3$ and $La_2Ti_2O_7$ oxide as anode catalyst in SOFC fueled with H_2S-containing methane. Electrochemical performance, impedance spectroscopy and other characterizations show that pure $BaTiO_3$ is a good anode catalyst for conversion of methane in SOFC, especially in H_2S-containing atmospheres. Compared with $SrTiO_3$ and $La_2Ti_2O_7$ samples, the $BaTiO_3$–based fuel cell has higher resistance to carbon deposition, better electrochemical performance and much higher stability during long term operation. A maximum power density of 135 mW cm^{-2} was achieved at 900 °C with 0.5% H_2S–CH_4 in a fuel cell having a 300 μm thick YSZ electrolyte. High catalytic activity for methane conversion, mixed electronic and ionic conductivity, and the surface basicity of $BaTiO_3$ unexpectedly provides promising performance as anodes in SOFC.

1. Introduction

Solid oxide fuel cells (SOFCs) have the advantages of high efficiency, low pollution, simplified mechanical and operating system and other features which make them very attractive for use in energy conversion systems [1,2]. SOFCs are suitable for many stationary power generation and back-up power applications. While very advantageous from a practical perspective, currently available fuels for SOFCs usually contain deleterious contaminants such as hydrogen sulfide (H_2S) or carbon monoxide (CO). A corrosive and extremely toxic gas, the concentration of H_2S present in natural gas ranges from trace amounts to more than 80% [3]. Natural gas which contains at least 50 ppm of H_2S is named sour natural gas, which needs to be treated before transportation and use due to the dangerous and corrosive nature of H_2S. Gas processing plants convert this toxic gas into elemental sulfur and water vapor via the well-established Claus process [4].

A SOFC with H_2S tolerance from 500 ppm up to several vol% is highly desirable because it would be able to utilize sour natural gas directly. H_2S is recognized as a problem in operating conventional SOFC as it can poison typical catalysts and is corrosive [5]. The most efficient H_2 SOFC catalyst (Ni–YSZ) to date is poisoned by H_2S rapidly either to form a sulfide or to poison the anode surface, which significantly degrades its activity for electrochemical oxidation of H_2 [6,7]. Therefore it is desirable to use an alternative sulfur tolerant anode material. The perovskite oxides that have mixed ionic and electronic conductivity (MIEC) are used as alternative anode materials for conversion of H_2S-containing feeds. Compared with metal-based anodes, such transition-metal-based perovskite oxides are less likely to promote coking or suffer from sulfur poisoning [8]. Various perovskite oxides, mostly based on doped strontium perovskite oxides, such as $CeSrVO_x$ [5], $LaSrVO_x$ [9–14], $LaYSrCrO_x$ [15], $LaSrCrMnO_x$ [16], $LaSrTiO_3$ [17,18] and $YSrTiO_3$ [19] have attracted attention as the anode materials for SOFC with H_2S-containing fuels since they show high electrical conductivity and chemical stability under the operating conditions. Some other double-perovskite structured materials, such as $SrMgMoO_x$ [20] or $SrMgMnMoO_x$ [21] also were considered as alternative anode materials. However, to date the electrocatalytic activity of these anode materials for SOFCs using H_2S-containing fuels, especially at high H_2S concentration, has not been applied widely.

Recently Vincent et al. found that doping of Ba into $LaSrTiO_3$ improved anode reaction activity [22]. Barium oxide based catalysts were found to be very active for the oxidation of methane, and there are many reports describing methane activation using Ba-based oxides, such as partial oxidation of methane (POM) [23,24], methane catalytic combustion [25,26], and oxidative coupling of methane (OCM) [27–29]. BaO significantly improved the catalytic

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performance of Gd_2O_3 for OCM [28]. Also it was found that BaO suppressed carbon deposition at the SOFC anode when methane was the fuel [30,31]. Carbon deposition is prevented effectively during the decomposition of CH_4 due to the basicity present at the anode surface. Among these, $BaTiO_3$ (BT) has been extensively studied for both partial oxidation and combustion of methane at high temperature since BT is very active in activation of both methane and oxygen [23,24,32–34]. Besides its application as catalyst, BT also has wide application as a major material in modern electronics technology [35].

In this study, we developed a BT anode catalyst with high activity for methane conversion that is stable in hydrocarbon- and H_2S-containing feeds. The stability and electrochemical properties of BT as anode material were investigated for use in various fuels, and during extended runs with H_2S and CH_4 fuels. For comparison, two other perovskite oxides, $SrTiO_3$ (ST) and $La_2Ti_2O_7$ (LT), also were tested under the same conditions. The intrinsic differences between these catalysts are discussed.

2. Experimental

2.1. Catalyst preparation

The various catalysts were prepared by solid state synthesis from high purity powdered precursors: $BaCO_3$ (Fisher, 99.4%), $SrCO_3$ (BDH, 99%), La_2O_3 (Alfa Aesar, 99.99%), and TiO_2(BDH, 99.5%). Equimolar amounts of the powders were weighed, M:Ti (M = Ba, Sr or La), and ball milled for 15 h to mix them uniformly. The mixed powders were calcined in air at 1200 °C for 5 h. Phase purity was determined using X-ray diffraction (Siemens D5000, Ni filtered, Co Kα1). YSZ was a commercial powder (TOSHO) and used as received.

2.2. Fuel cell fabrication

Fuel cells were fabricated using commercial YSZ disks (FCM, “fuelcellmaterials.com”) as electrolyte, 300 m thick and 25 mm in diameter. The anode and cathode were intimate mixtures of equal weights of YSZ with pore-precursor PMMA and with the various titanate oxide catalysts (anode), or with commercial strontium doped lanthanum manganite (LSM) powders (cathode), respectively. The mixtures were finely powdered in a planetary ball milling machine, then dispersed in glycerine to form the corresponding electrode inks. Each electrode ink was screen printed onto the opposed faces of the electrolyte to form a membrane electrode assembly (MEA) with circular 1 cm^2 anode electrodes, and then sintered 1 h at 1200 °C. After sintering the combination of anode and electrolyte, 1 cm^2 platinum paste was painted on the cathode side and gold paste was painted on the anode side, then both pastes were sintered in-situ to form current collectors. An

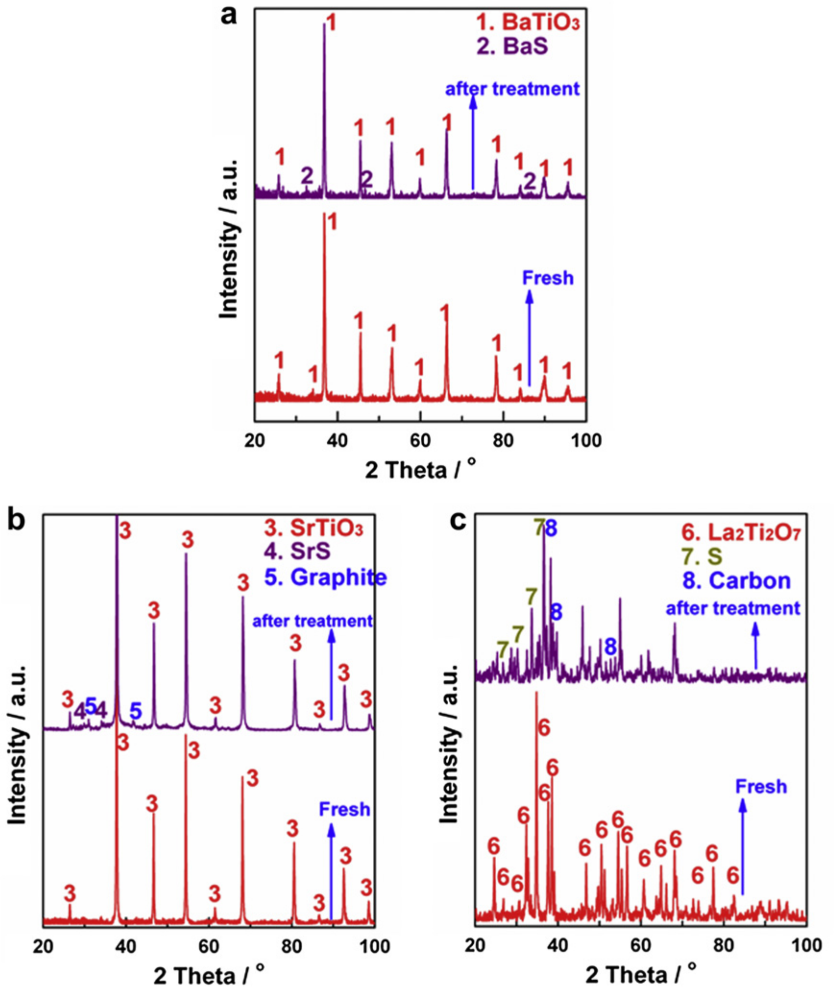

Fig. 1. XRD patterns (Ni filtered, Co Kα1) of (a) $BaTiO_3$; (b) $SrTiO_3$ and (c) $La_2Ti_2O_7$ before and after calcining in 0.5% H_2S–CH_4 at 950 °C for 10 h.