Electrochemical performance of direct carbon fuel cells with titanate anodes

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A B S T R A C T

For power generation, fuel cells offer a number of advantages over conventional thermal power stations such as high efficiency, low pollution and CO_2 emissions and the ability to be used as distributed power generation sources at load centres. Amongst these, the direct carbon fuel cell (DCFC) offers many additional attributes which include near 100% fuel utilisation, 100% theoretical efficiency and almost pure CO_2 in the flue stream requiring no costly separation from other gases. In the solid oxide electrolyte based DCFC, for effective oxidation of solid fuel, the anode plays a significant role. In particular, the mixed ionic electronic conducting ceramics offer the potential of shifting reaction sites from anode/electrolyte interface to fuel/anode interface thus making it easier for oxidation of solid fuel which unlike gaseous fuels cannot penetrate in the porous structure of the anode. In this paper, in view of a good mix of ionic and electronic conductivity and the possibility of higher catalytic activity of Co doped lanthanum strontium titanates for hydrocarbon fuel oxidation, these materials have been investigated as a potential anode for use in a DCFC. The performance was evaluated with solid carbon, H_2 and CO as fuel feeds. The performance has been compared with $Sr_{0.86}Y_{0.08}TiO_3$ and $La_{0.3}Sr_{0.7}TiO_3$. The effect of adding a noble metal catalyst in small quantities has also been reported to facilitate the carbon oxidation reaction.

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1. Introduction

The increasing scarcity of energy sources and inefficient methods of their utilisation to produce power are of utmost concern for the present and future generations. Coal and natural gas (NG) are the main fuels used in power generation plants. Coal fired power plants are not only less efficient (about 30% coal to electricity conversion efficiency), but also contribute to the pollution due to the particulate matter and NO_x/SO_x, and greenhouse gas emissions. In general, coals from different parts of the world contribute between 0.8 and 1.3 kg CO_2 emissions for each kW-h of electricity produced, thus becoming a major contributor to the greenhouse gas emissions. Although there are global efforts to develop technologies for CO_2 capture and sequestration, this remains an audacious challenge, considering the large quantity of CO_2 produced per annum by coal fired power plants, the energy required for CO_2 separation from flue gases (about 25% energy penalty leading to further drop in overall plant efficiency), and costs associated with its capture and sequestration. According to IEA, in 2011, coal accounted for 45% of the energy related CO_2 emissions of the total 32 giga tonnes generated globally, followed by 35% from oil and 20% from NG [1]. There are over 860 billion tonnes of coal reserves worldwide and

are estimated to last for more than 100 years at the current rate of production and consumption [2]. Therefore, more efficient technologies need to be developed to prolong the life of these reserves and to reduce pollution and CO_2 emissions.

Fuel cells generally offer a number of advantages over thermal power stations for power generation. These include high energy density and efficiency, low pollution and CO_2 emissions, distributed power generation with the potential of utilising heat at demand centres (combined heat and power generation - CHP) [3]. Most major fuel cell systems are based on gaseous fuels (hydrogen, CO, CH_4) and suffer from low fuel utilisation (typically in the 80-85% range).

A significant progress has been made in polymer electrolyte membrane fuel cell technology especially for transport applications. However, the commercialisation is largely hindered by the almost non- existence of the hydrogen storage and transportation/distribution infrastructure. Both molten carbonate (MCFC) and solid oxide fuel cells (SOFCs) can be operated directly on natural gas (NG) with *in-situ* or external reforming and offer electric efficiencies in the range of 45-60% [4].

Although there are many residual issues related to life time and cost for most types of fuel cells, a large number of units ranging in size from a few kW to MW are currently in operation.

Another type of fuel cell which has attracted attention more recently, utilises solid carbon in the anode chamber of the fuel cell and is commonly referred to as the direct carbon fuel cell. It, offers

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many additional attributes which include, near 100% fuel utilisation, 100% theoretical efficiency and almost pure CO_2 in the flue stream requiring no separation from other gases. Practical efficiencies in the 65-70% range have been predicted leading to halving the fuel utilisation and CO_2 emissions compared with conventional thermal power plants [5]. Several different types of direct carbon fuel cells (DCFC) are under consideration as detailed in recent reviews on this technology [5–7]. Amongst various types of DCFCs, solid oxide electrolyte based systems, where no corrosive media (molten salts or metal) is used, are attracting more attention in particular. However, the delivery of solid carbon to active interfacial sites for direct carbon oxidation remains a major challenge and the anode plays a key role.

Traditionally Ni-YSZ is the preferred anode material for SOFCs. However, it is susceptible towards coking with hydrocarbon fuels and sulphur contamination leading to a drop in the fuel cell performance with time. The coking leads to deposition of carbon in the microspores of the anode, blocking triple phase boundaries for fuel cell reactions and obstructing diffusion of the fuel and product gases. The carbon deposition can occur either by hydrocarbon cracking or via Boudouard reaction given below.

$$CH_4 \rightarrow C + 2H_2 \tag{1}$$

$$2CO \rightarrow C + CO_2 \tag{2}$$

In DCFCs it has been generally agreed that apart from the direct carbon oxidation at the anode/electrolyte interface, CO produced by the reverse Boudouard reaction (2) or partial electrochemical oxidation of carbon at the anode/electrolyte interface (reaction 3 below), also contributes to the power generated as a result of its further oxidation at the anode/electrolyte interface to carbon dioxide (reaction 4) as follows [5]:

$$C + O^{2-} \rightarrow CO + 2e^- \tag{3}$$

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \tag{4}$$

Therefore, it is critical to select an anode material that is stable in CO atmosphere and also makes carbon and all CO produced by either of the above reactions (reverse Boudouard reaction (2) or reaction (3)) react efficiently as per reaction (4).

In a previous publication, the role of mixed electronic and ionic conducting anode to allow solid carbon to react at the anode/electrolyte interface was discussed and why it is critical to optimise the ionic and electronic conducting properties of the material [8]. Over the past decade, a number of ceramic anodes have been investigated for hydrocarbon based SOFCs which are resistant to coking and tolerant to impurities in hydrocarbons [9–14]. Among these anodes, titania and ceria based materials are particularly promising. The ceria based anodes possess a good catalytic activity and oxygen storage capacity, however, the electronic conductivity of ceria based anodes is low. To improve the conductivity, a conducting phase such as Ni or Cu may be added to the anode. Such anodes have shown a great promise for direct oxidation of methane, and also have been found to be tolerant to sulphur impurities [15,16]. With humidified hydrogen, power densities upto 470 mW/cm^2 have been reported for gadolinia-doped ceria ($Ce_{0.6}Gd_{0.4}O_{1.8}$) in electrolyte supported fuel cells at 800 °C [17]. The La or Y doped strontium titanates (LST or SYT) anodes possess excellent stability in reducing environments and have been reported to be compatible with yttria stabilised zirconia (YSZ) electrolyte [18,19]. Depending on synthesis and reducing conditions, these anodes have an excellent electronic conductivity (as high as 5000 S/cm) [17]. Similar to ceria based anodes, titanates posses good tolerance for sulphur and H_2S impurities making them viable option for hydrocarbon fuels without the need for complete desulphurisation of the fuel feed. Mukundan et al. have reported that YSZ

electrolyte supported fuel cell with $La_{0.4}Sr_{0.6}TiO_3$ (LST)/YSZ composite anode operated at 800 °C for over 8 hours in 1% H_2S without significant degradation [20]. Although titanates have shown good stability as anodes and reasonable electronic conductivity, the inferior catalytic activity towards fuel oxidation is the major issue for practical applications. Various methods such as infiltration with precious group and base metals and/or mixing with catalytically active phase like ceria, have been employed to improve the catalytic performance of these anodes [21–24]. Another approach to improve the electrochemical performance is by B-site doping with transition metals such as Co, Fe or Ni [25,26]. B-site doping of LST not only improves the catalytic activity but also improves oxygen vacancy concentration because of partial substitution of Co or Ni at the titanium site which in turn also improve the ionic conductivity [25]. Under the reducing atmosphere and at SOFC operating temperatures it is possible that some of the doped transition metal may exolute from the perovskite creating additional defects in the host lattice. These exoluted metallic particles may act as catalysts improving the electrochemical performance of SOFC anode [24]. Recently Tsekouras et al. observed a dramatic improvement in the catalytic activity of electrodes in solid oxide electrolyser operation due to improved ionic conductivity and partial exsolution of Fe and Ni in the form of nanophase metallic particles from $La_{0.4}Sr_{0.4}Fe_{0.06}Ti_{0.94}O_{2.97}$ and $La_{0.4}Sr_{0.4}Ni_{0.06}Ti_{0.94}O_{2.9}$ under reducing conditions [27]. For fuel cell applications, Li et al. investigated electrical properties of the Co doped LST anode. These authors, for 6 mol% Co doping at B-site in $La_{0.3}Sr_{0.7}TiO_3$, reported an ionic conductivity up to 0.015 S/cm with electronic conductivity of about 50 S/cm at 800 °C in 5% H_2-N_2 mixture [28]. However, no electrochemical performance data were given.

In view of a good mix of ionic and electronic conductivity, and the possibility of higher catalytic activity of Co doped LST for hydrocarbon fuel oxidation, in this paper, we have investigated $La_{0.3}Sr_{0.7}Ti_{0.93}Co_{0.07}O_3$ (LSCT) as a potential anode for use in a DCFC where carbon is the fuel feed. In addition to solid carbon fuel, we also report the electrochemical performance of this anode with H_2 and CO fuel feeds. The effect of adding a noble metal catalyst in low loading amounts has also been investigated. Furthermore, we have investigated the performance of another two anodes namely $Sr_{0.86}Y_{0.08}TiO_3$ (SYT) and $La_{0.3}Sr_{0.7}TiO_3$ (LST) which have been studied previously in detail in gaseous fuels [18,19] and compared their performance with LSCT anode for solid carbon as the fuel feed.

2. Experimental

2.1. Anode powder synthesis

The starting powders for $La_{0.3}Sr_{0.7}Ti_{0.93}Co_{0.07}O_3$ (LSCT) anode were synthesized by combustion of particles incorporated polymeric precursor. Reagent grade nitrates were used as source compounds for all cations except for Ti^{4+}. For Ti^{4+}, titania nanoparticles were synthesized by sol gel hydrolysis of titanium isopropoxide and used as the source compound [29]. The calculated amounts of respective nitrates were dissolved in deionised water and ethylene glycol was used as the chelating agent. The solution was polymerized followed by addition of dispersion of titania nanoparticles in deionised water under continuous stirring and heating at 80 °C. The resulting solution was left in an evaporating dish at 80 °C until a viscous cake was formed. This was followed by firing at 400 °C to burn off organic matter. The material was ground in mortar/pestle to a fine powder which was then fired at 900 °C to obtain single phase perovskite. Two further titanate compositions $Sr_{0.88}Y_{0.12}TiO_3$ (SYT) and $La_{0.3}Sr_{0.7}TiO_3$ (LST) were synthesized using the same method for comparison.