



Silver–praseodymium oxy-sulfate cermet: A new composite cathode for intermediate temperature solid oxide fuel cells



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HIGHLIGHTS

- A novel Ag–Pr₂O₂SO₄ composite cathode was developed.
- High oxygen storage capacity facilitated gaseous oxygen to be adsorbed.
- A highly active property towards oxygen reduction reactions was achieved.
- The highest power density reached 1.5 W/cm² at 800 °C.
- High stability of the cell at 800 °C under load was maintained for 24 days.

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ABSTRACT

Ag–Pr₂O₂SO₄ is identified as a promising new composite material to enhance the cathodic oxygen reduction reaction in solid oxide fuel cells. Ag–Pr₂O₂SO₄ was studied in terms of synthesis, stability of Pr₂O₂SO₄ in CO₂, and electrochemical behavior as a cathode. The performance of the composite cathode was assessed as a function of temperature by A.C. impedance using a symmetrical cell arrangement in oxygen. The global performance of an anode-supported fuel cell Ag–Pr₂O₂SO₄/CGO/NiO–CGO was also assessed, the highest power density being 1.5 W cm^{−2} at 800 °C. A longevity test of this cell performed at 800 °C under load for 24 days demonstrated high stability with Ag–Pr₂O₂SO₄ cathode.

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1. Introduction

Solid oxide fuel cells (SOFCs) are devices of commercial and environmental importance that effectively convert the chemical energy of fuels directly to electricity. They combine advantages of environment-friendly electricity generation with fuel and oxidant flexibility, opening up an extensive range of potential applications, such as stationary power for isolated areas, public transportation power, and even portable power. Nonetheless, the marketability of these applications depends on the achievement of stable fuel cell operation at minimal cost. In order to attain this requirement a reduction in the SOFC working temperature, to at least 600–800 °C, has been suggested as desirable [1–5]. The benefits of lowering the operating temperature include fast start-up of the system, an

increase in materials stability and a reduction in cost. However, with the decrease in the working temperature, the polarization resistances of the electrode and of the electrode/electrolyte interface can increase dramatically [4]. This is because the catalytic oxidation/reduction reactions on the surface of the electrode and the ionic transport within the electrode slow down and take major responsibility for impaired power density of the whole fuel cell [4].

In order to deal with this challenge, a variety of perovskite-type ABO₃ and Aurivillius-type phases have been developed and improved as potential intermediate temperature SOFC cathodes [2,6]. With respect to the typical ABO₃ perovskite structure, strontium-doped lanthanum manganite (La_{1-x}Sr_xMnO_{3-δ}, LSM) mixed with yttria-stabilized zirconia (ZrO₂)_{0.92}(Y₂O₃)_{0.08}, a classical ionic conductor, has traditionally been the composite cathode of choice. Here (ZrO₂)_{0.92}(Y₂O₃)_{0.08} provides oxygen ionic conductivity while the LSM phase predominantly works as an electronic conductor [7]. Single-phase mixed ionic and electronic conductors

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(MIECs) such as $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF) and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ (SSC) have also been suggested to reduce the cathodic interfacial polarization resistance at lower temperatures [8,9]. Shao and Haile [10] replaced the rare-earth elements (Ln) with alkaline-earth (Ba) and presented $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) as a new cathode material for reduced-temperature SOFC operation. The power densities of cells using this cathode reached values as high as 1010 mW cm^{-2} at $600 \text{ }^\circ\text{C}$ when operated with humidified hydrogen as the fuel and air as the oxidant [10].

For the Aurivillius-type structures, it was found that the $\text{Bi}_2\text{Cu}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ (known as BICUVOX10) showed very good electrochemical performance at $600 \text{ }^\circ\text{C}$ [11–14]. However, its disadvantage of low electronic transference number requires the addition of an electronically superior conducting phase to form a composite. For example, Liu and Xia [6,15] mixed silver powder with BICUVOX10, to provide the required electronic conductivity offering a peak power density of 443 mW cm^{-2} at $550 \text{ }^\circ\text{C}$. Tao et al. prepared a core–shell Au–BICUVOX10 cathode fabricated on top of a finger-like CGO electrolyte to increase the triple phase boundary (TPB) length, and achieved a power density of 470 mW cm^{-2} at $550 \text{ }^\circ\text{C}$ by this modification [16,17].

Such previous work has, therefore, shown that a suitable cathode for an intermediate temperature fuel cell should offer sufficient electronic and ionic conductivities, either as a single-phase MIEC or as a composite of two phases to provide the MIEC nature. In an unconventional departure from previous materials for this goal, the current study offers a completely new composite cathode for SOFCs based on combination of silver particles and porous praseodymium oxy-sulfate, $\text{Pr}_2\text{O}_2\text{SO}_4$. Such oxy-sulfate materials have traditionally been suggested as oxygen storage materials due to their large oxygen storage capacity [18]. Although there are various mechanisms suggested to be involved in the oxygen storage in $\text{Pr}_2\text{O}_2\text{SO}_4$, for example that the distortion of the oxygen sub-lattice generates some mobile oxide-ions and that the change in the oxidation states of $\text{Pr}^{3+}/\text{Pr}^{4+}$ can catalyze oxygen exchange, it is the redox ability of sulfur that is mainly attributed for the high levels of oxygen storage capacity [19].

Due to the ability of the Ln oxy-sulfates to store oxygen [20–22], they have been applied as catalysts for the high-temperature water–gas shift reaction [23], and for anaerobic catalytic CO oxidation [24]. In the present work, a novel composite cathode of Ag– $\text{Pr}_2\text{O}_2\text{SO}_4$ is prepared and carefully characterized in terms of stability, microstructure and electrochemical behavior. In this composite it is envisaged that silver will function as the electronic component, while the $\text{Pr}_2\text{O}_2\text{SO}_4$ phase may provide mobile oxygen species and fast oxygen exchange [25]. The performance of an anode-supported fuel cell of composition Ag– $\text{Pr}_2\text{O}_2\text{SO}_4$ /CGO/NiO–CGO was assessed, including longevity testing of an optimized cell operated at $800 \text{ }^\circ\text{C}$ for a period of 24 days under load.

2. Experimental

2.1. Preparation and characterization of composite cathode

$\text{Pr}_2\text{O}_2\text{SO}_4$ oxy-sulfate powder was prepared using a solid-state reaction method using praseodymium (III) sulfate octahydrate $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ (Alfa Aesar). Before heating, this precursor was ground in an agate mortar and pestle. Then the powder was annealed at $850 \text{ }^\circ\text{C}$ for 5 h in air (heating and cooling rates of $10 \text{ }^\circ\text{C min}^{-1}$). After pyrolysis, the formed $\text{Pr}_2\text{O}_2\text{SO}_4$ oxy-sulfate powder was intimately mixed with silver powder (particle size of $\sim 1.3 \text{ } \mu\text{m}$, Alfa Aesar) in order to prepare Ag– $\text{Pr}_2\text{O}_2\text{SO}_4$ mixtures (20, 40, 50, 60 and 80 wt.% of silver). X-ray diffraction (XRD) patterns were collected using a Bruker D-8 Advance diffractometer with a CuK_α ($\lambda = 0.15405 \text{ nm}$) radiation, at increments of $0.02^\circ 2\theta$ and

counting time of 2 s per step. Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) were carried out using the Netzsch Jupiter instrument in dry air atmosphere with heating and cooling rates of $5 \text{ }^\circ\text{C min}^{-1}$. Before sintering, oxy-sulfate and composite powders were pressed uniaxially under 50 MPa into bars of diameter 10 mm and length 40 mm, and then pressed isostatically under 600 MPa during 30 min using Hiperbaric 55 hydrostatic press. The bars were sintered at $900 \text{ }^\circ\text{C}$ for 24 h. The level of porosity was determined by a “slice and view” approach using a FEI Helios 450S focused ion beam scanning electron microscope. Dilatometric characterization was performed by a MI-900 Michelson Laser Interferometer. The total conductivity of the bulk composites was measured by a 4-probe DC technique in air.

2.2. Preparation and characterisation of symmetrical assemblies and fuel cells

The $\text{Pr}_2\text{O}_2\text{SO}_4$ oxy-sulfate and silver powders (60:40 wt.%) were mixed with terpineol in a NOAH NQM-2 planetary ball-milling machine at 400 rpm for 2 h followed by ultrasonication for 1 h, to break possible agglomerates. $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ (CGO) powder (Alfa Aesar) was isostatically pressed at 200 MPa during 1 min into disks of 1.5 mm thickness and 10 mm diameter, followed by sintering at $1600 \text{ }^\circ\text{C}$ for 5 h in air (heating and cooling rates of $1.5 \text{ }^\circ\text{C min}^{-1}$). Thin Ag– $\text{Pr}_2\text{O}_2\text{SO}_4$ films (0.264 cm^2 of effective area) were deposited over the CGO disk using a WS-650-23 Laurell spin coater at 2000 rpm for 30 s, to provide a cathode electrode thickness of around $20 \text{ } \mu\text{m}$. For formation of symmetrical cathode–electrolyte–cathode assemblies, this process was repeated on the reverse side of the pellet after drying in air. The symmetrical assemblies were then annealed at $900 \text{ }^\circ\text{C}$ for 5 h in air, with heating and cooling rates of $1.5 \text{ }^\circ\text{C min}^{-1}$. For the complete fuel cell, CGO electrolyte powder was spin-coated onto partially-sintered ($900 \text{ }^\circ\text{C}$, 5 h) NiO/CGO (70 wt.% of NiO, Alfa Aesar) disks with thickness of 0.9 mm and diameter of 15 mm, followed by sintering at $1300 \text{ }^\circ\text{C}$ for 10 h in air. The Ag– $\text{Pr}_2\text{O}_2\text{SO}_4$ (40 wt.% of silver) composite was then spin-coated onto the center of electrolyte of the prepared anode/electrolyte assembly, as described for the symmetric cell. The reference electrode was prepared by attaching and firing platinum paste onto the electrolyte around the cathode (Ag– $\text{Pr}_2\text{O}_2\text{SO}_4$) as a ring. The cell morphology was observed using a Jeol JSM-6500F scanning electron microscope (SEM). The impedance spectra of the symmetric assembly were taken from 550 to $800 \text{ }^\circ\text{C}$ in oxygen using Princeton 273A potentiostat/galvanostat in the frequency range of 0.01 Hz–1 MHz using a signal amplitude of 50 mV. The power output of the fuel cell was monitored with the Arbin SOFC Testing System from 550 to $800 \text{ }^\circ\text{C}$ with wet hydrogen (3% of H_2O) as fuel and oxygen as oxidant with the same feeding rates of 80 ml min^{-1} . Long-term stability testing was performed at $800 \text{ }^\circ\text{C}$ with a load of 0.2Ω , a constant load corresponding to the maximum power density, with gas feeding rates of 50 ml min^{-1} . The respective current was recorded automatically every 10 min, to a total of 24 days.

3. Results and discussion

3.1. Structural, dilatometric and conductivity study

Fig. 1 shows the TG and DSC profiles of the precursor $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ upon heating in the temperature range $25\text{--}1350 \text{ }^\circ\text{C}$. Three main weight loss events can be observed. Before $550 \text{ }^\circ\text{C}$, a 18% weight loss can be correlated to the dehydration of $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ to $\text{Pr}_2(\text{SO}_4)_3$, as confirmed by complementary XRD studies (Fig. 2a). From 550 to $850 \text{ }^\circ\text{C}$, $\text{Pr}_2(\text{SO}_4)_3$ remained stable, whereas after $850 \text{ }^\circ\text{C}$ another 20% weight loss occurred identified by XRD to be that of transformation of $\text{Pr}_2(\text{SO}_4)_3$ into $\text{Pr}_2\text{O}_2\text{SO}_4$. At

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