

**CERIUM-MODIFIED DOPED STRONTIUM  
TITANATE COMPOSITIONS FOR SOLID  
OXIDE FUEL CELL ANODES AND  
ELECTRODES FOR OTHER  
ELECTROCHEMICAL DEVICES**

REFERENCES TO RELATED APPLICATIONS

This application is a divisional of U.S. patent application Ser. No. 10/427,866, filed May 1, 2003, now U.S. Pat. No. 7,670,711 which claims the benefit of U.S. Provisional Application No. 60/377,527, filed May 3, 2002, each of which is hereby incorporated by reference herein in their entireties.

GOVERNMENT RIGHTS

This invention was made with Government support under Contract Number DE-AC0676RLO1830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

BACKGROUND OF THE INVENTION

The present invention relates to novel oxide electrode materials comprising cerium-modified doped strontium titanate and methods for making and using same. Oxide electrode materials in accordance with the invention find advantageous use in solid oxide electrolyte electrochemical devices such as, for example, solid oxide fuel cells, electrolyzers, electrochemical sensors and the like.

As a background to the invention, electrochemical devices based on solid oxide electrolytes have received, and continue to receive, significant attention. For example, electrochemical fuel cell devices are believed to have significant potential for use as power sources. In addition, electrolyzers have received significant attention for the production of hydrogen from water.

Fuel cell devices are known and used for the direct production of electricity from standard fuel materials including fossil fuels, hydrogen, and the like by converting chemical energy of a fuel into electrical energy. Fuel cells typically include a porous anode, a porous cathode, and a solid or liquid electrolyte therebetween. In operation, gaseous fuel materials are contacted, typically as a continuous stream, with the anode (also referred to as the "fuel electrode") of the fuel cell system, while an oxidizing gas, for example air or oxygen, is allowed to pass in contact with the cathode (also referred to as the "air electrode") of the system. Electrical energy is produced by electrochemical combination of the fuel with the oxidant. Because the fuel cells convert the chemical energy of the fuel directly into electricity without the intermediate thermal and mechanical energy step, their efficiency is substantially higher than that of conventional methods of power generation.

Solid oxide fuel cells (SOFCs) employing a dense ceramic electrolyte are currently considered as one of the most attractive technologies for electric power generation. In a typical SOFC, a solid electrolyte separates the porous metal-based anode from a porous metal or ceramic cathode. Due to its mechanical, electrical, chemical and thermal characteristics, yttria-stabilized zirconium oxide (YSZ) is currently the electrolyte material most commonly employed. At present, the anode in a typical SOFC is made of nickel-YSZ cermet, and the cathode is typically made of doped lanthanum manganites, lanthanum ferrites or lanthanum cobaltites. In such a fuel cell, an example of which is shown schematically in FIG. 1, the fuel flowing to the anode reacts with oxide ions to produce

electrons and water. The oxygen reacts with the electrons on the cathode surface to form oxide ions that migrate through the electrolyte to the anode. The electrons flow from the anode through an external circuit and then to the cathode. The movement of oxygen ions through the electrolyte maintains overall electrical charge balance, and the flow of electrons in the external circuit provides useful power.

Because each individual electrochemical cell made of a single anode, a single electrolyte, and a single cathode generates an open circuit voltage of about one volt and each cell is subject to electrode activation polarization losses, electrical resistance losses, and ion mobility resistant losses which reduce its output to even lower voltages at a useful current, a fuel cell assembly comprising a plurality of fuel cell units electrically connected to each other to produce the desired voltage or current is required to generate commercially useful quantities of power.

Limited by the conductivity of YSZ, SOFCs typically operate at high temperatures, such as, for example, 650-1000° C. This allows flexibility in fuel choice and results in suitable fuel-to-electricity and thermal efficiencies; however, high temperatures impose stringent requirements on the materials selection for other components of the fuel cell or fuel cell assembly.

The material used as an SOFC anode must possess a high electronic or preferably mixed ionic and electronic conductivity. It must also exhibit sufficient catalytic activity towards the reaction proceeding on the electrode surface to minimize polarization losses. Also necessary are adequate porosity for gas transport, and good chemical and mechanical compatibility with the electrolyte and interconnect. In addition, the anode must be thermally stable, i.e., stable over a wide range of temperatures. Another desirable feature is that an anode should be stable over a rather wide range of oxygen partial pressures (pO<sub>2</sub>), such as, for example, in the low oxygen partial pressure prevalent in the fuel gas inlet as well as in the more oxidizing conditions (high oxygen partial pressure) at the fuel outlet. Furthermore, if the SOFC is to operate on unreformed hydrocarbons, the anode should also possess a high catalytic activity for hydrocarbon oxidation without carbon deposition. When combined with fabrication considerations, these requirements make the development of suitable new anode materials a challenging task.

As stated above, for SOFCs with a YSZ electrolyte, a nickel-YSZ cermet is currently the favored anode material. Properties of nickel-based composite anodes have been profoundly investigated, and their reliability and robustness for stationary power applications has been established over a long-term operation on clean pre-reformed fuel (hydrogen). However, additional constraints must be placed on the anode material in order to economically bring SOFC technology into more advanced designs including, for example, power sources for motor vehicles and auxiliary power units, and other applications that involve intermittent power demands, intermittent usage and nonusage, and thus repeated heating and cooling cycles. In particular, for applications requiring frequent thermal cycling, anode stability in oxidizing conditions at high temperatures is necessary. In this regard, during system heat-up and cool-down, an anode that is tolerant of oxidizing environments withstands thermal cycling without the need for protecting the anode by hermetic sealing or flowing of an inert or reducing gas.

Due to the high nickel content of Ni-YSZ (typically around 40 vol % nickel) or other nickel-based composite materials, and the ease with which nickel is oxidized into nickel oxide in oxidizing atmospheres, conventional nickel-based anodes suffer structural damage when cycled without a protective