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Inorganic binder-containing composite cathode contact materials for solid oxide fuel cells

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HIGHLIGHTS

► Addition of inorganic binder to SOFC contact materials enhances bonding.
► Enhanced bonding after low-temperature cure.
► Acceptably low ASR achieved for select binder compositions.

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ABSTRACT

The feasibility of adding inorganic binder to conventional SOFC cathode contact materials in order to improve bonding to adjacent materials in the cell stack is assessed. A variety of candidate binder compositions are added to LSM. The important properties of the resulting composites, including ASR, reactivity, and adhesion to LSCF and MCO-coated 441 stainless steel are used as screening parameters. The most promising CCM/binder composites are coated onto MCO-coated 441 coupons and anode-supported button cells with LSCF cathode, and tested at 800 °C. It is found that a LSM-644A composite displayed excellent initial performance and promising stability. Indeed, addition of binder is found to improve bonding of the CCM layer without sacrificing CCM conductivity.

1. Introduction

Assembly of solid oxide fuel cell (SOFC) stacks typically involves mechanically and electrically connecting a number of cells and interconnects in series. Connection of the cathode to the interconnect (or coating on the interconnect) is usually accomplished by compression of the stack using an external load frame, and is often aided by the use of a cathode contact material (CCM). The CCM is an electrically conductive material, and is applied as a paste or ink during stack assembly to form a continuous layer or discrete contact pads. The CCM provides electrical connection between the cathode and interconnect, and can also serve to improve in-plane conduction over the area of the cathode. Fig. 1 indicates placement of the CCM in the fuel cell stack. Often, the CCM is simply a thick layer of the electrocatalyst used in the cathode. [1] For example, a thin LSM-YSZ cathode layer optimized for electrochemical activity can be covered with a thick LSM CCM layer optimized for gas transport and electrical conductivity. A significant limitation of this approach, however, is that most cathode compositions require firing at high temperature (>1100 °C) to achieve good sintering. [2] The use of ferritic stainless steel as the interconnect material limits the firing temperature to 1000 °C or lower. In practice, therefore, using a cathode catalyst CCM in conjunction with a stainless steel interconnect results in low CCM layer strength and minimal adhesion at the CCM/interconnect or CCM/cathode interface.

Efforts to decrease the required sintering temperature through doping [3], control of the defect structure [3,4], and addition of glass [5] have had some success. In the present work, we assess the merit of adding inorganic binder to the CCM in order to improve bonding without sacrificing acceptable conductivity of the resulting binder-ceramic composite.

2. Approach

The CCM composition must fulfill the following requirements:

- high electronic conductivity
- sintering/bonding at 1000 °C or lower
- good CTE match to other cell components

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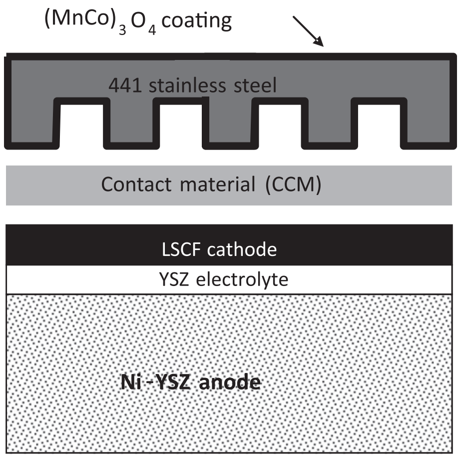

Fig. 1. Schematic representation of CCM placed between SOFC cell and coated stainless steel interconnect.

- mechanical strength within the CCM layer and at the interfaces to cathode and interconnect

Our approach is to fabricate composite mixtures of SOFC cathode material and inorganic binder. Conventional CCM pastes use a cathode material to achieve both bonding and electrical contact. In contrast, the approach we take is to separate the functions of electrical contact and mechanical (or chemical) bonding. Inorganic binders are frequently used in the manufacture of high-temperature adhesives, mortars, plasters, and cements. Ceramic–inorganic binder composites are widely used as seals for SOFCs, because they wet to other SOFC materials and bond after curing at relatively low temperature (often room temperature to about 350 °C), producing mechanically robust seals. [6] For example, SOFC ceramic adhesive sealants typically comprise alumina or zirconia filler particles and a polyphosphate-, silicate-, or aluminosilicate-based inorganic binder suspended or dissolved in water. The binder functions by crosslinking, polymerization, or curing various polyphosphate, polysialate, polysiloxo, poly(sialate–siloxo), silicate etc. groups. The adhesive may be applied as a wet paint or paste, and hardens and cures upon drying or heating. The heating temperature (if any) is much lower than the temperature required to sinter the ceramic filler particles. For example, alumina requires >1500 °C to sinter, but alumina-filled ceramic adhesive can be cured at <400 °C to produce a hard, dense, well-adhered coating or bonding layer. Such adhesives are commercially available from Aremco and Cotronics (exemplary products include 552T, 503T, 644A, 644S, 830, 542, 794, 795, 797). The goal is to prepare a CCM composition that displays improved bonding via addition of inorganic binder, without sacrificing conductivity or long term stability of the resulting mixture.

Initially, single commercially-available inorganic binders are mixed with LSM. These mixtures are characterized for conductivity, mechanical properties, and reaction between the LSM and binder. The most promising binder/LSM mixtures are applied to MCO-coated 441 steel coupons and tested for area-specific resistance (ASR). Those mixtures showing the best ASR are then applied to button cells with Pt mesh current collectors and operated at 800 °C to determine performance and stability.

3. Experimental methods

3.1. Materials

LSM powder was purchased from Praxair. Aqueous inorganic binder solutions were purchased from Aremco (542, 830, 644A, 644S, 552T) and Cotronics (794, 795). Metal powders were supplied by Ametek (434), Novamet (316 flakes, dendritic Ni 525), and Alfa Aesar (NiCr).

3.2. XRD and SEM

XRD (Philips X'Pert) was used to check reaction between binder and LSM. The XRD trace for pure LSM was compared to those for mixtures of LSM and binders after curing at 360 °C, and after sintering at 1000 °C for 1 h in air. Powders and ASR specimens were imaged with SEM (Hitachi S4300SE/N).

3.3. Paste fabrication and initial assessment

Metal or LSM (1000 °C coarsened) powders were mixed with the amount of each binder required to make a workable paste (typically 4 g powder and ~1.5 g aqueous binder solution). The pastes were then applied to an alumina substrate, cured according to the manufacturers' instructions (typically 360 °C), and heated to 800 °C for 2 h. Upon cooling, the resistance was estimated with a multi-meter, and the bonding was qualitatively assessed by scraping the cement with a blade. In certain cases, load at failure was determined using stud-pull tests, described below.

3.4. ASR measurements

Specimens for ASR measurements were prepared according to the geometry in Fig. 6. Various CCM inks were prepared by mixing the powders with aqueous inorganic binder solutions using a planetary mixer (Thinky). 441 stainless steel coupons were coated with MCO by screenprinting at Pacific Northwest National Laboratory (PNNL). CCM layers were then brush painted onto the MCO layer, dried under a heat lamp and cured in air at according to the manufacturers' instructions (typically 360 °C), followed by a 1 h hold at 800 °C. Pt paste (Heraeus CL11-5349) and Pt mesh (Alfa Aesar 10283) were applied as current collectors on the CCM layers, and sintered at 800 °C. Pt mesh was spot-welded to the 441 coupon. The ASR specimens were then subjected to 500 mA current for 200 h at 800 °C in air. DC current was applied in a 4-probe configuration using a Biologic VMP3 potentiostat.

3.5. Mechanical analysis

Interfacial adhesion was assessed using an epoxy-stud pull tester (Quad Group Sebastian V). CCM/binder pastes were printed and sintered onto LSCF-coated YSZ disks and MCO-coated 441 coupons.

3.6. Cell testing

Anode supported button cells with LSCF cathode and GDC barrier layer (MSRI) were used. The cathode was coated with CCM paste and then cured as above. Pt mesh current collector was attached with Pt paste (Heraeus) to both the anode and CCM (or bare LSCF cathode in the case of no-CCM baseline cells). The cells were mounted to alumina tubes with Aremco 552 sealant and tested at 800 °C with 97%H_2/3%H_2O fuel. After obtaining initial impedance spectra, the cells were operated at 300 mA cm^{-2} for roughly 250 h. DC current was applied in a 4-probe configuration using a Biologic VMP3 potentiostat.

4. Results and discussion

4.1. Proof of concept: metal-binder composites

Aremco 552 is a common SOFC sealant, containing alumina filler particles and aqueous sodium silicate binder. Alumina-free thinner