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Reaction of steam and methane over novel YSZ –LaB_6 composites and nickel-YSZ cermets

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Aims

Current SOFC Ni-YSZ cermet anodes suffer from a number of problems when exposed to methane-containing fuels at typical operating temperatures. These include; carbon deposition, nickel sintering and poisoning by sulfur present in the methane supply; ultimately these processes result in degradation in fuel cell performance.

In this study our goal is to explore an alternative anode material that is resistant to carbon deposition and sintering. The system under investigation is a composite that is fabricated from sintering LaB_6 and 8mol%YSZ under an argon atmosphere. A comparison in catalytic activity is made with a number of Ni-8mol %YSZ cermets using temperature programmed methods under CH_4 and CH_4-H_2O atmospheres.

Material fabrication

The Ni-YSZ cermets where fabricated using Ni electroless plating (EP), with either N_2H_4 or NaH_2PO_2 as reducing agent, and Ni nano powder with a commercial YSZ powder. The Ni content was around 40% following sintering under 5% H_2/Ar at 1000°C for 2 hrs (Table 1). The YSZ-LaB_6 composites were made by sintering required mixtures of commercial YSZ and LaB_6 powders in Ar at 1350°C for 2 hrs (Table 2). XRD of the as-made composites indicate that they are not single phase; ZrB_2 is present, unreacted LaB_6 and $LaBO_3$/$La(BO_2)_3$ type phases depending on the proportions of starting materials used to fabricate the composite, while the Ni cermets showed metallic Ni and the support (patterns not shown).

Table 1. 40% Ni cermets

cermet A	Ni/NiO- γ-Al_2O_3 EP (N_2H_4) 34.4 m^2 g^{-1}
cermet B	Ni/NiO-YSZ EP (NaH_2PO_2) BET 4.2 m^2 g^{-1}
cermet C	Ni/NiO-YSZ EP (N_2H_4 BET) 4.5 m^2 g^{-1}
cermet D	Ni/NiO-YSZ (Ni nano powder) 4.0 m^2 g^{-1}

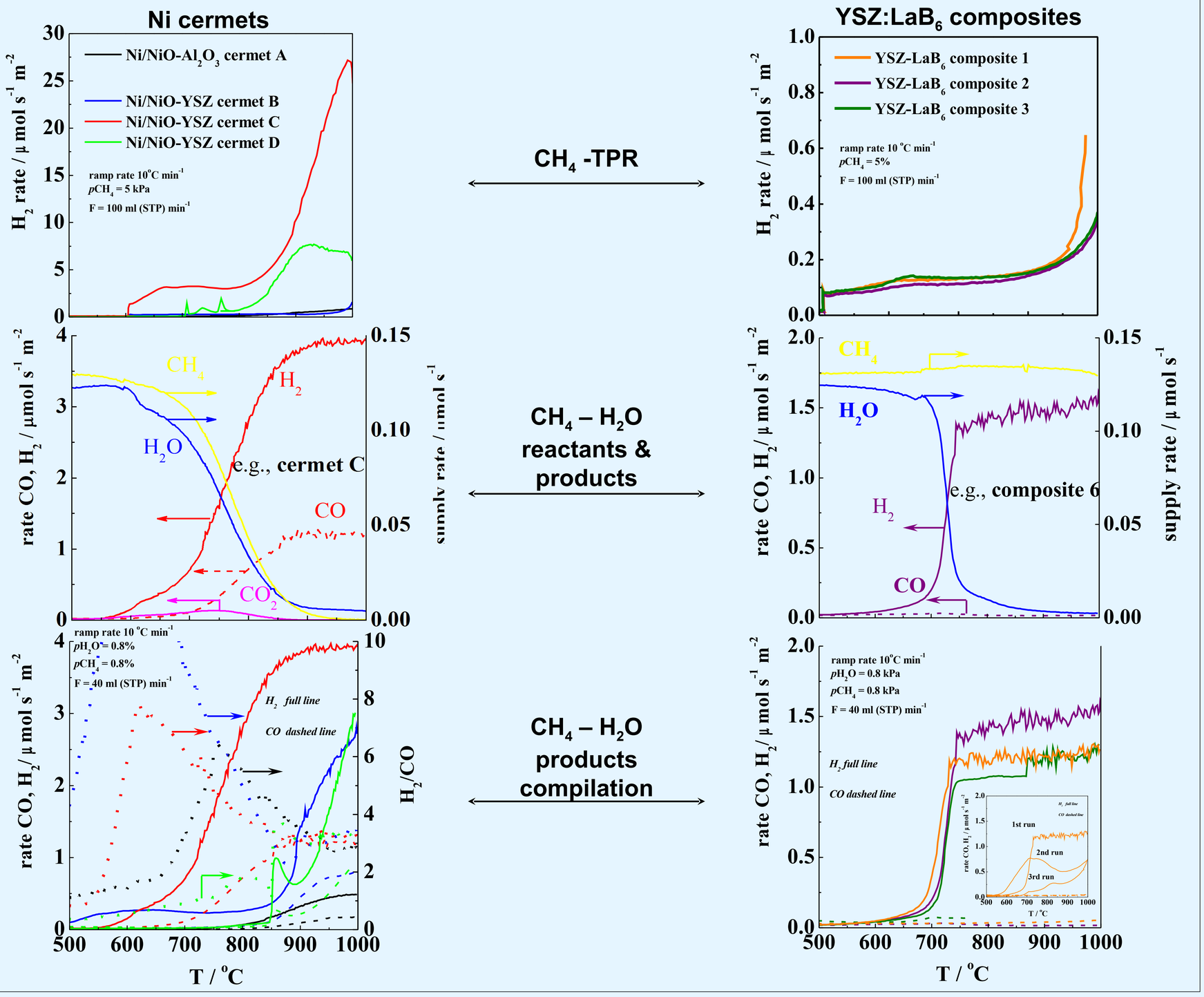
Table 2. YSZ-LaB_6 composites

COMP1	YSZ:LaB_6 10:90 0.9 m^2 g^{-1}
COMP2	YSZ:LaB_6 50:50 1.3 m^2 g^{-1}
COMP3	YSZ:LaB_6 70:30 2.2 m^2 g^{-1}

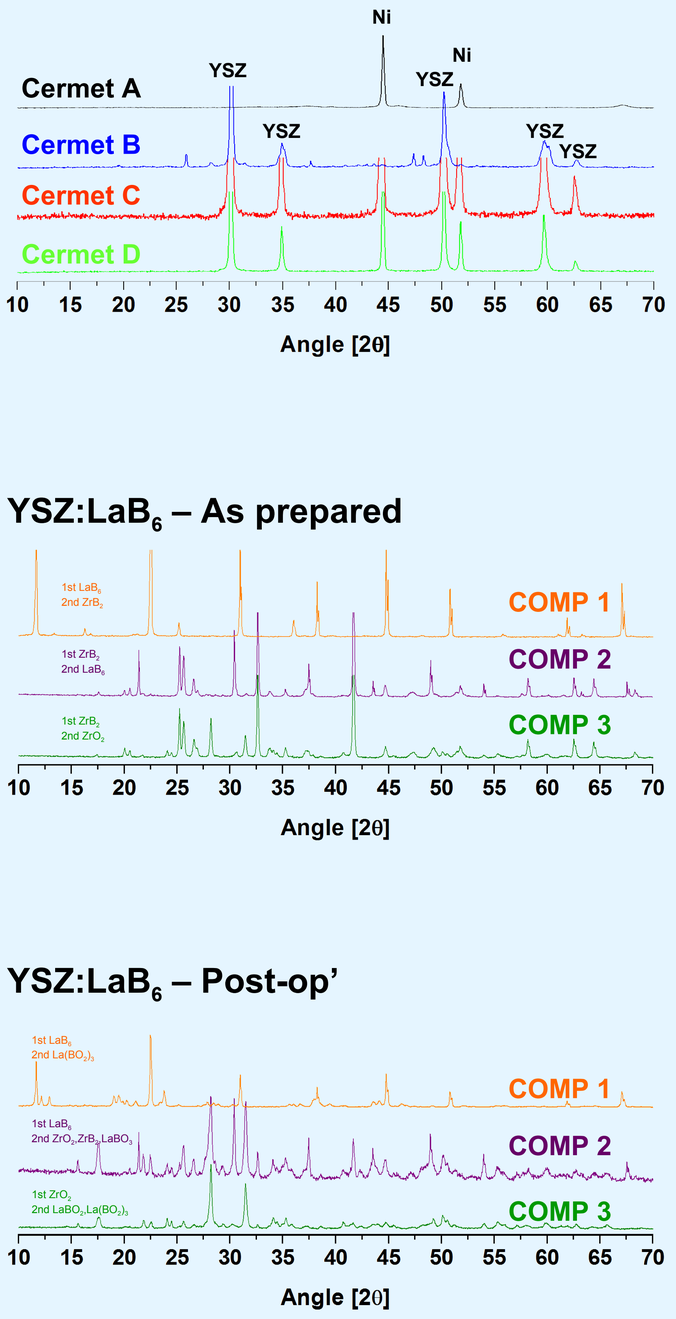
Material catalytic testing

Catalytic tests were carried on an automated catalytic testing rig comprising of; gas-supply and control, microreactor and online mass spectrometer. Dry CH_4 was supplied at 5 kPa (in He) for the CH_4-TPR tests (600-1000°C) and 0.8 kPa CH_4 and 0.8 kPa H_2O were co-fed (in He) for steam reforming (50-1000°C) . Typically 50 ±3 mg of fresh sample was used and a heating rate of 10°C min^{-1} to the final set point temperature. The sample was then cooled to room temperature in He for post operation analysis.

Results on dry and steam methane reforming



Powder x-ray diffraction



Discussion

The initial investigation with CH_4-TPR indicated that cermets B and D would be the best candidates for steam reforming with methane. The Ni cermets steam reform the methane to mostly H_2 and CO with some coking at lower temperature as indicated by the H_2 to CO ratio. Using N_2H_4 as reducing agent in the EP deposition of Ni onto the YSZ crystals produced the most active cermet of those studied here. The YSZ-LaB_6 composites in comparison are poor at cracking the CH_4 molecule to produce H_2 but are very active for water splitting to give H_2 as the only gas-phase product. The methane during the reforming tests is inert although some coke deposition at high temperature is likely. During three methane-steam cycles there was still sign of activity for water splitting but progressively this reduced. XRD indicates "unzipping" of the composites.

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