

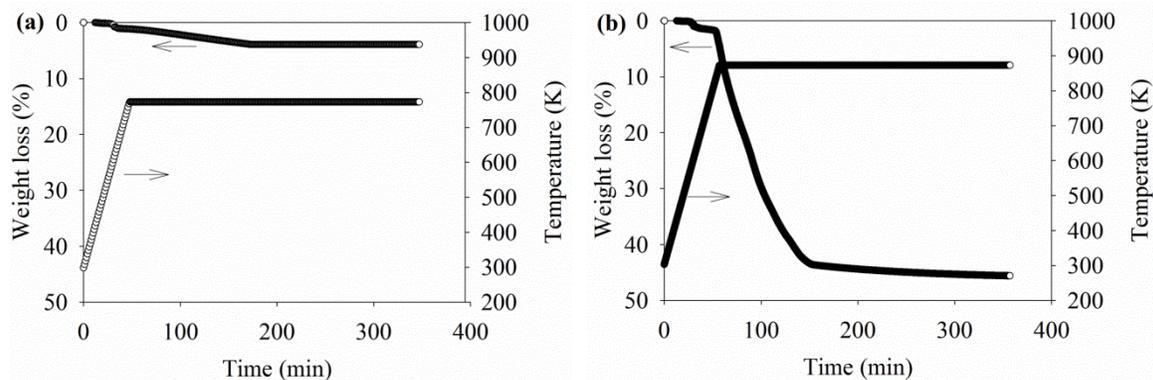
Supporting Information

Barium oxide promoted Ni/YSZ solid-oxide fuel cells for direct utilization of methane

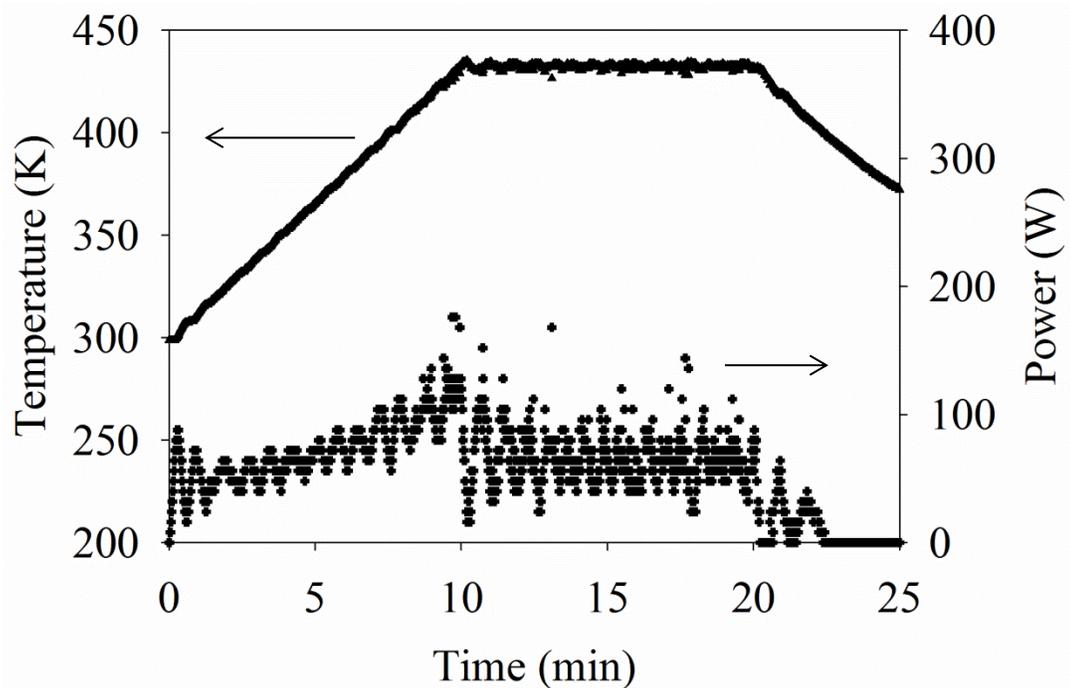
By Shamiul Islam,^a and Josephine M. Hill ^{*a}

Department of Chemical and Petroleum Engineering, University of Calgary,
2500 University Dr. NW, Calgary, Alberta, T2N 1N4, (Canada)
E-mail: (islas@ucalgary.ca)

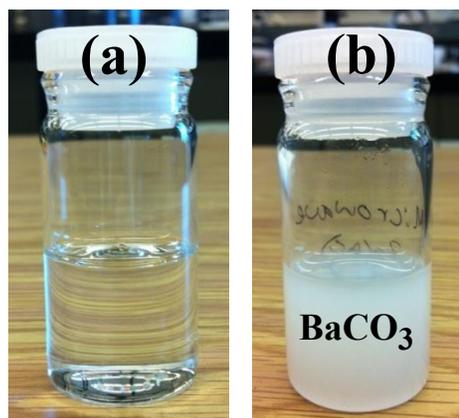
TGA analysis of $\text{Ba}(\text{NO}_3)_2$ powder was carried out at (a) 773 K and (b) 873 K in flowing N_2 with a ramp rate of 10 K min^{-1} and a holding time of 5 h at the respective temperatures. At 773 K, $\text{Ba}(\text{NO}_3)_2$ barely decomposed to its oxide and the weight loss corresponds to only 4%. However, when the temperature was increased to 873 K, a weight loss of 43% is observed, which was close to the theoretical loss of 41% for the decomposition of $\text{Ba}(\text{NO}_3)_2$ to its oxide (BaO). Thus a calcination temperature of 873 K was chosen for the thermal decomposition of impregnated $\text{Ba}(\text{NO}_3)_2$ particles to BaO in the sintered NiO/YSZ anodes.



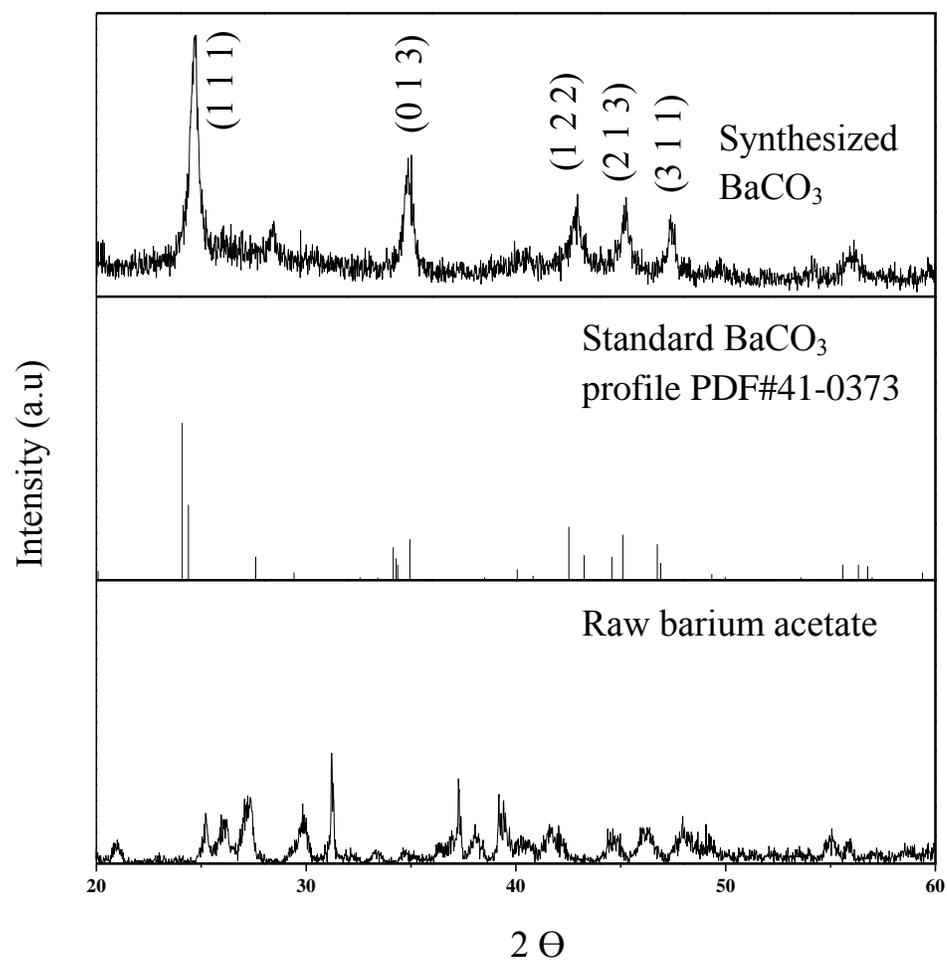
Supplementary Fig. S1. Thermogravimetric analysis of $\text{Ba}(\text{NO}_3)_2$ powder. (a) 773 K and (b) 873 K.



Supplementary Fig. S2. In-situ measurement of the temperature and power during microwave experiments.

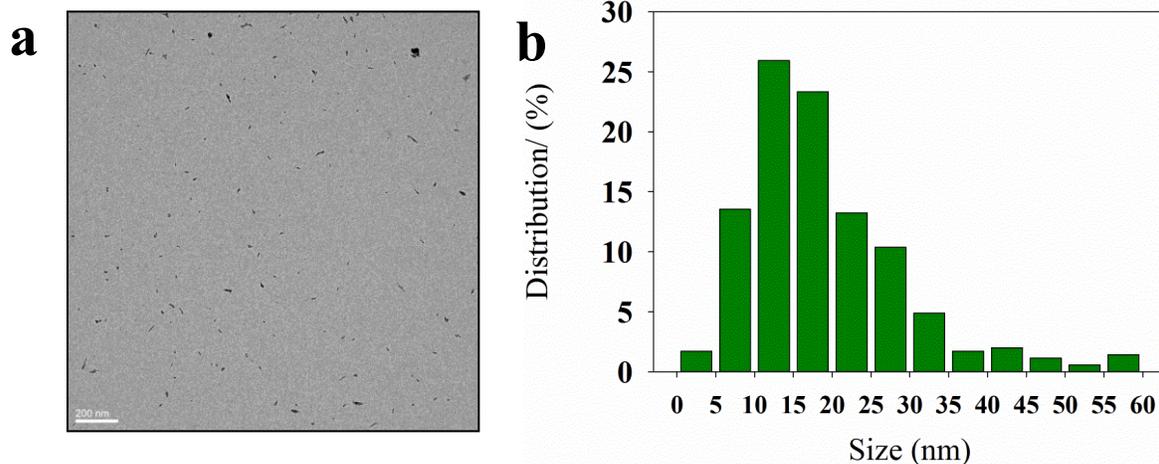


Supplementary Fig. S3. $\text{Ba}(\text{CH}_3\text{COO})_2$ solution (a) before and (b) after microwave irradiation at 433 K.



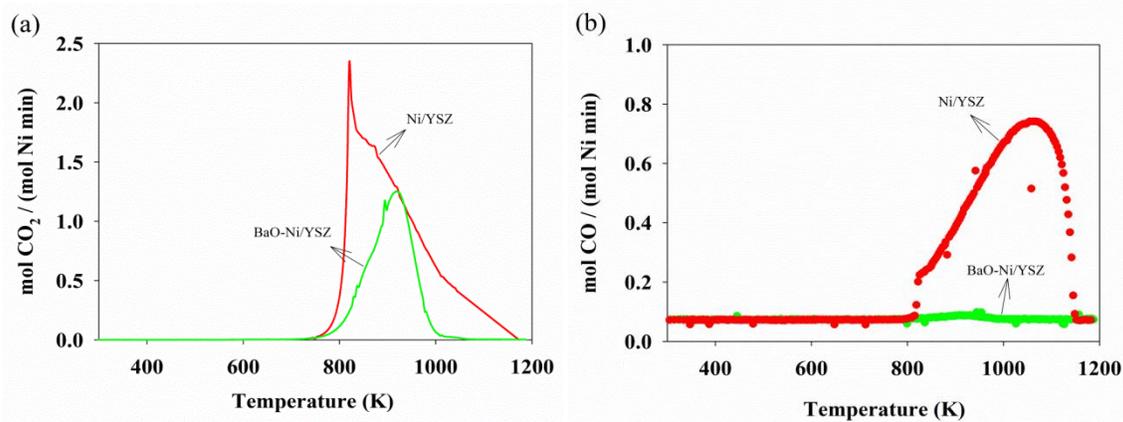
Supplementary Fig. S4. X-ray diffraction patterns of raw barium acetate, synthesized BaCO₃, and the JCPDS profile for BaCO₃.

In order to observe the morphology of the BaCO_3 powder, TEM analysis was performed using a drop of BaCO_3 suspension on a Cu-grid and the morphology of the particles and particle size histogram are shown in Fig. S5. The dark contrast in (a) was the BaCO_3 nanoparticles, which were elongated in shape, while the grey contrast was the Cu-grid. A relatively narrow particle size distribution of BaCO_3 was obtained with 86% of the nano-particles less than 30 nm in size.



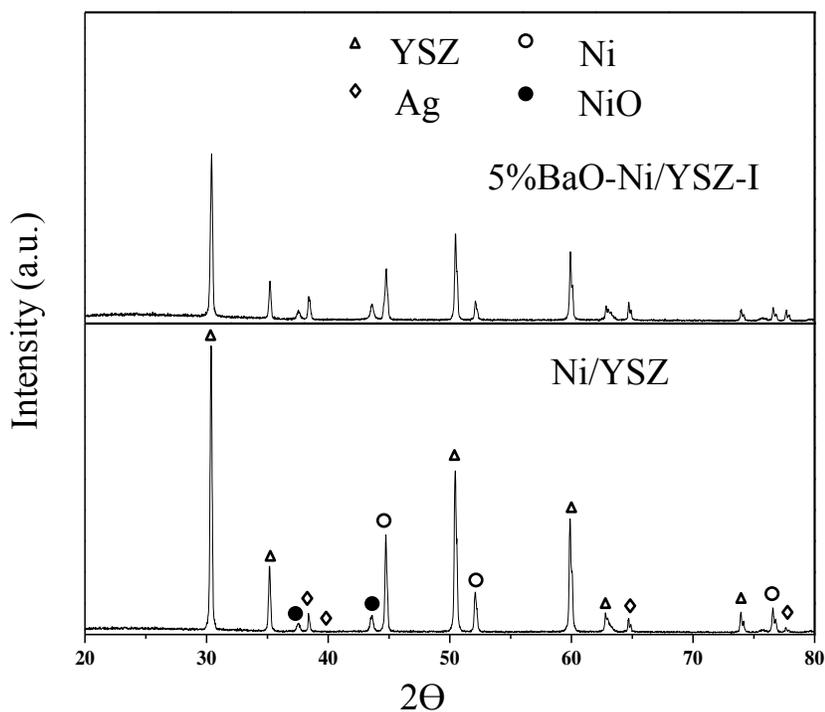
Supplementary Fig. S5. TEM micrograph of BaCO_3 powder and the corresponding particle size distribution.

NiO/YSZ anodes (with and without 5%BaO) sintered on YSZ pellet was exposed to dry CH₄ for 6 h at 1073 K in a flow reactor and TPO was performed thereafter to analyze the carbon accumulation. Prior to testing in dry CH₄, the NiO of the cell was reduced to Ni in-situ in H₂ for 1 h at 1073 K. As seen in Fig. S5a, the total amount of deposited carbon is lower for the 5%BaO-Ni/YSZ-I anode compared to the Ni/YSZ anode indicating that BaO covered the surface of Ni and likely reduced the activity of Ni for CH₄ cracking reaction. The TPO peak for CO₂ was very broad as the amount of supplied O₂ was not sufficient to completely oxidize the carbon. Consequently, carbon oxidized partially and a peak for CO can be seen in Fig. S5b.



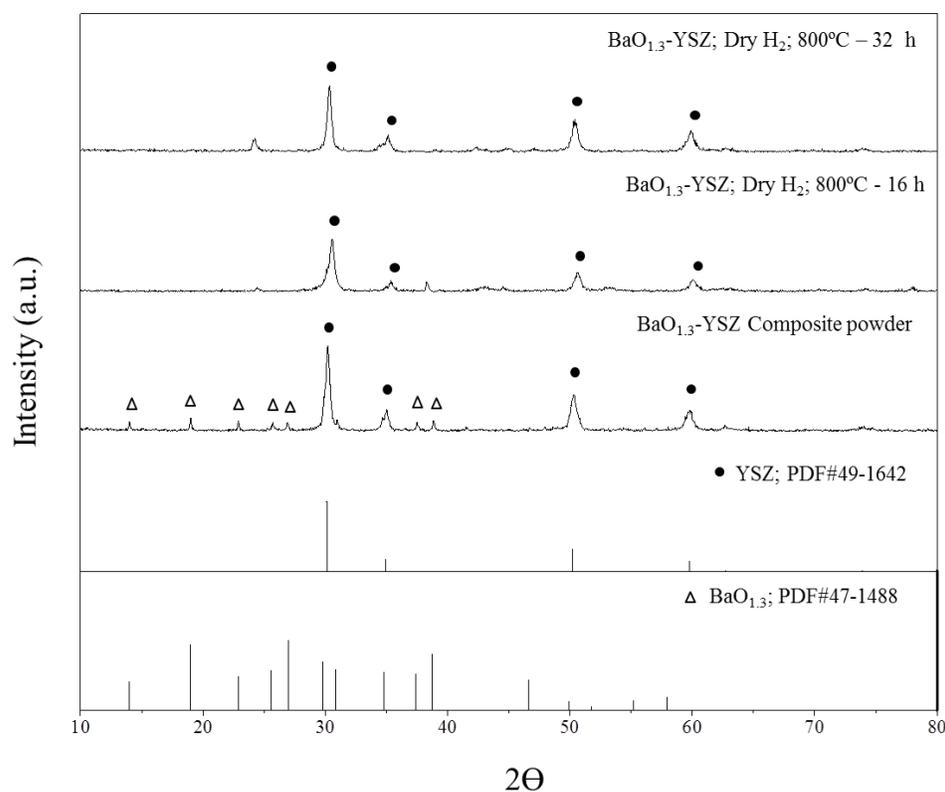
Supplementary Fig. S6. TPO profiles showing the carbon accumulation in terms of (a) CO₂ and (b) CO production on Ni/YSZ and 5%BaO-Ni/YSZ-I anodes after exposure to dry CH₄ for 6 h at 1073 K.

The XRD patterns were obtained after performing galvanostatic tests for 8 h at 20 mA cm^{-2} under dry CH_4 at 1073 K. The XRD pattern of the 5%BaO-Ni/YSZ-I cell was very similar to that of the Ni/YSZ cells. In both the cases, the peaks from YSZ, Ni, NiO and Ag were observed. For the peak identification of YSZ, Ni, NiO and Ag, the PDF profiles of 37-4113, 04-0850, 22-1189 and 04-0783 were used, respectively. The peak for BaO was not observed in the spectra as the amount of BaO was likely below the detection limit of the XRD equipment. No peak for BaCO_3 was observed in the spectra. A minor peak of NiO was identified which indicates that Ni at the anode was partially oxidized during the galvanostatic testing while the peak of Ag appeared due to the presence of Ag paste on the anode surface.



Supplementary Fig. S7. XRD patterns of the Ni/YSZ and 5%BaO-Ni/YSZ-I cells after galvanostatic tests at 20 mA cm^{-2} under dry CH_4 at 1073 K.

A composite powder of BaO (Sigma-Aldrich, USA) and YSZ (TOSOH, TZ-8Y, Japan) (wt. ratio 25:75) was exposed to dry H₂ in a flow reactor for 16 h at 1073 K and XRD was performed on the samples before and after testing. The weight ratio of BaO to YSZ of 25 to 75 was chosen so that the peaks for BaO could be observed in XRD analysis. The results are shown in Fig.S8. The peaks in the composite powder match the reference patterns of YSZ (PDF#49-1642) and BaO_{1.3} (#47-1488). The as received BaO powder was nonstoichiometric with excess oxygen in it. After testing the composite powder in H₂ at 1073 K, the peaks of BaO_{1.3} disappeared while the peaks at 24.5 and 38.3 could not be identified with certainty. The intensity of the peak at 24.25 increased as the testing time increased from 16 h to 32 h. This analysis suggests that BaO is not chemically stable with ZrO₂ at 1073 K, which is consistent with the SEM images in Fig. 4, in which it appeared that the BaO had diffused in to ZrO₂.



Supplementary Fig. S8. XRD patterns of the BaO_{1.3}-YSZ composite powder before and after exposure to dry H₂ for 16 h and 32 h at 1073 K and the standard PDF for YSZ and BaO_{1.3}.