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Role of Dopants in fine-tuning the electrical and catalytic properties of Barium Niobate Perovskites towards high-temperature electrolyzer application

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Perovskite materials are used for high temperature electrochemical applications such as solid oxide fuel cells (SOFC) and electrolyzers due to their tunable conductivity and catalytic activity. However, high temperature operation poses significant challenges in both fabrication and durable operation that is further complicated by the operating environment. We studied barium niobates with various A and B site dopants. These doped niobates showed enhanced thermochemical stability in SOFC relevant conditions and catalytic activity towards methane activation. The redox behavior of the $Nb^{4+/5+}$ couple seem to be at a key reason behind this redox stability while the size and electronegativity of the dopants affect the electrical properties. The chemical stability was analyzed by TGA measurements followed by analysis of the perovskite powders using PXRD measurements. Impedance measurements were utilized to analyze their electrical conductivity. Our results demonstrate doped barium niobates as a promising candidate for stable operation in high temperature electrochemical applications.

Introduction

Thermochemical stability is one of the key characteristics for any new materials being developed for high temperature electrochemical applications such as solid oxide fuel cells (SOFC) and solid oxide electrolyzers (SOE). Anode materials should possess redox stability over a very wide oxygen partial pressure. This requirement is further exacerbated under carbonaceous gas environments due to coke and carbonate formation that destroys the surface catalytic and electrical properties and render the cell inactive (1, 2).

Recent discoveries of new resources of natural gas has made methane one of the highly abundant and inexpensive fuel of choice (3, 4). However, during the extraction process, methane is often flared or released to the atmosphere through leaks, at wells without proper pipeline infrastructure, and at wells with insignificant quantities of methane (5, 6). Hence, research on the direct conversion of methane to value added higher hydrocarbon products has attracting renewed interest. In this respect, electrochemical oxidative coupling of methane (EOCM) has not been explored extensively where recent reports indicate the potential of EOCM to increase the selective conversion of methane to ethylene in SOE cells (7–11). However, chemical stability and durability of these cells remains a challenge.

We recently reported Mg and Fe codoped barium niobates for EOCM application where it showed good methane activation and chemical stability properties under these conditions (12). However, their electrical conductivity at 900 °C was only about 17 $mScm^{-1}$ that restricted the overall achievable current densities. Hence, in this study, we varied the dopants such as Ca and Y along with Fe to study the role of dopants on their electrical conductivity. Here, we present our electrical conductivity and chemical stability results along with methane activation properties of the Ca, Fe, and Y coped barium niobates.

Experimental

The perovskite $BaCa_{0.33}Nb_{0.67-(x+y)}Fe_xY_yO_{3-\delta}$, was produced using solid-state synthesis methods. Initially, the metal oxide and metal carbonate precursors were weighed in stoichiometric ratios to produce 7 g of $BaCa_{0.33}Nb_{0.67-(x+y)}Fe_xY_yO_{3-\delta}$ with x values of 0.00, 0.17, 0.25, 0.33, and y values of 0 and 0.1 corresponding to BCN, BCNF17, BCNF25, BCNF33, BCNY, and BCNFY respectively. The precursors were mixed in a planetary ball mill for 6 hours in IPA, dried and sintered at 1000 °C for 24 hours. The resulting powders were further ball milled for 6 hours in IPA, dried and pelletized in a 15 mm die and sintered at 1420°C for 24 hours. The pellets were utilized for conductivity measurements and crushed powders used for PXRD and TGA measurements.

TGA measurements were carried out using TA Q600 SDT instrument in air and in pure methane environments with flow rate of 10 mL min^{-1} in the temperature window of 25 to 900 °C at a heating and cooling rate of 5 °C min^{-1} and held at 900 °C for 1 h. X-ray diffraction measurements were done in a PANalytical Xpert Pro instrument equipped with a Goebel mirror monochromator using Cu Kα radiation and operating at 40 kV and 40 mA on a zero-background holder. Electrical conductivity measurements by impedance analysis was carried out on the pellets using Gamry Reference 600+ instrument. The pellets were first sputter coated with Pt on both sides followed by a layer of Pt applied by ink paint brushing. The Pt coated pellets were sintered at 900 °C for 10 hours.

Results and Discussion

Figure 1a shows the PXRD patterns of the six prepared materials. All samples form the perovskite structure with a Fm-3m space group (13). PXRD patterns obtained for these samples after exposure to pure methane in a TGA set up at 900 °C for an hour is given in Figure 1b. There are no additional peaks observed in methane exposed samples indicating the chemical stability of all prepared compositions in carbonaceous conditions. Experiments aimed at preparing the parent barium niobate ($BaNbO_3$) resulted in multiple phases. The calculated Goldschmidt tolerance factor value of 1.023 for $BaNbO_3$ predicts this single phase instability. Hence no further attempt is made to prepare the $BaNbO_3$ single phase composition.

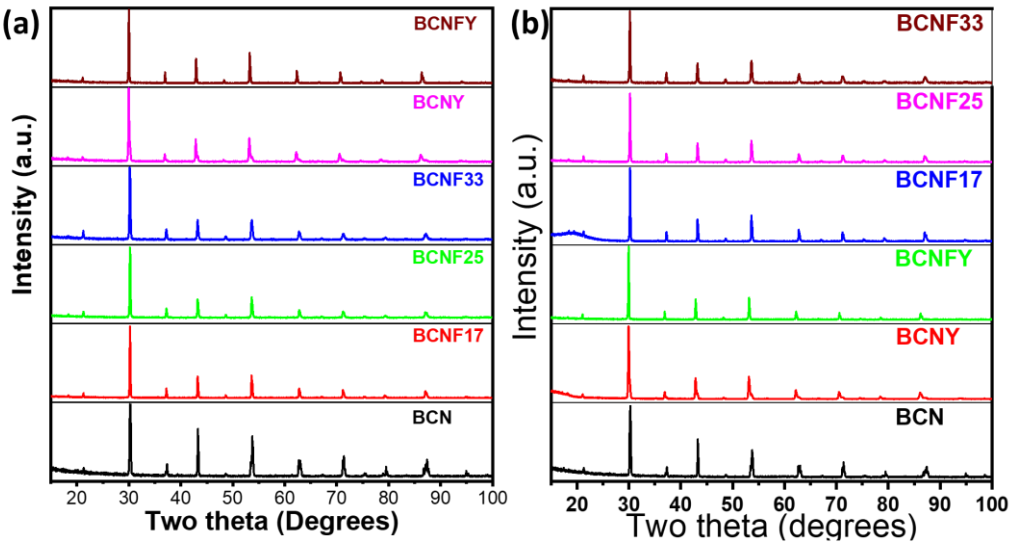

Figure 1. PXRD patterns obtained for all the prepared compositions (a) as prepared, (b) after methane exposure at 900 °C for an hour.

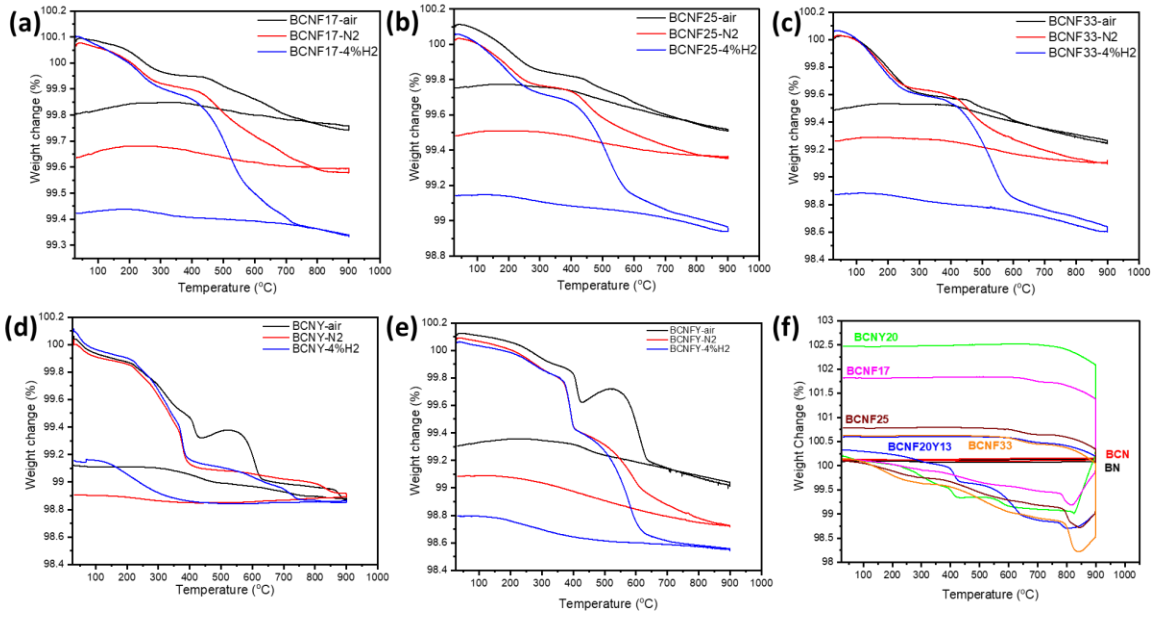

Figure 2. Thermogravimetric analysis graphs obtained under different gas atmospheres for (a) BCNF17, (b) BCNF25, (c) BCNF33, (d) BCNY, (e) BCNFY, and (f) under pure methane for all prepared compounds.

TGA plots obtained under different gas environments such as air, N_2, and 4% H_2 balanced in N_2 are given in Figure 2a to 2e for the five prepared compounds. BCN did not show any significant weight loss or gain and is not presented in the figures. Figure 2a to 2c clearly show that with increasing Fe doping, the weight loss is linearly increasing in the BCNF perovskites. Similarly, the weight loss is linearly increasing in the order of

4%H_2/N_2>N_2>air. The difference in weight loss between air and 4%H_2/N_2 could indicate the amount of oxygen loss due to reduction in metal components oxidation state. The estimated difference in weight loss between air and 4%H_2/N_2 at 900°C is 0.44, 0.525, ad 0.497% for BCNF17, BCNF25, and BCNF33 respectively. This oxygen loss would be compensated by either the reduction of Fe^{3+} to one of its lower oxidation states such as Fe^{2+} or $Fe^{(0)}$. The other possible option is for Nb^{5+} to reduce to Nb^{4+}. A simple calculation with an assumed starting oxygen stoichiometry of 3 in all the three compounds indicate that about 4 to 5% of the Fe^{3+} will be reduced to $Fe^{(0)}$ or about 15% of Fe^{3+} will be reduced to Fe^{2+}. However, our preliminary XPS results (data not shown here) show all the Fe^{3+} to remain Fe^{3+} before and after exposure to 4%H_2/N_2 in the TGA measurements. However, the Nb ion could be reduced from Nb^{5+} to Nb^{4+} and compensate for the oxygen loss as the other two metal components Ba and Ca are not expected to reduce under these conditions. Note that there is little difference in the Shannon Nb^{4+} and Nb^{5+}ionic radii (0.68 vs 0.64Å) or M-O bond length (2.03 vs 1.99Å) (14). Further measurements using XPS and XAS are currently underway to further understand the reduction process and provide more information on the interesting chemical stability of these materials. In the case of Y doped samples, both BCNY and BCNFY, there is a small weight gain peak between 400°C to 700°C in air that is not observed under N_2 or 4% H_2/N_2. This could be due to oxygen incorporation in vacancy sites. In BCNY, the overall weight loss at 900 °C remains nearly the same whereas in the Fe containing BCNFY, there is a linear drop similar to BCNFs. Further measurements are required to confirm the exact nature of the weight gain peak in Y doped samples and the role of Y and Fe in controlling the physical and electrical properties of these materials. TGA under methane for the prepared perovskites (Figure 2f) did not show significant weight gain and retained the crystalline structure without any impurity peak formation (Figure 1b). Our experiments with another EOCM catalyst, $Sr_2Fe_{1.5}Mo_{0.5}O_{6-d}$ under similar conditions showed about 40 to 60% weight gain for comparison along with complete decomposition of the crystal structure.(7)

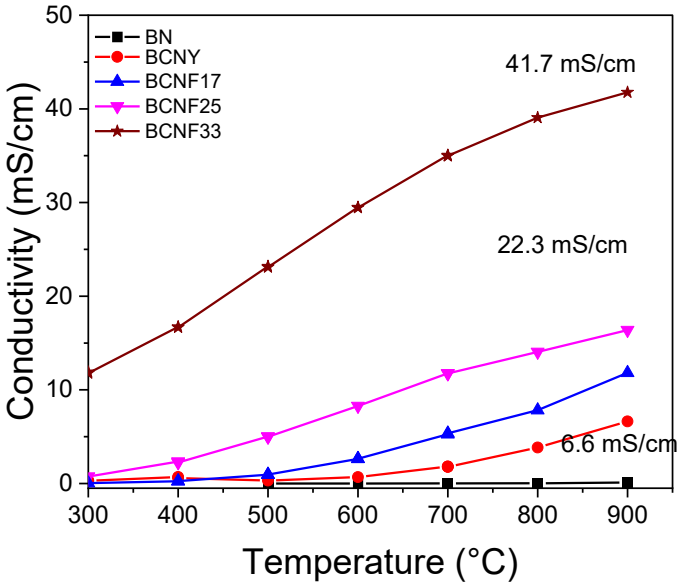

Figure 3. Conductivity values obtained for the different doped barium niobates in the temperature range of 300 °C to 900 °C.

Electrical conductivity values obtained by impedance measurements in the temperature range of 300 °C to 900 °C is given in Figure 3. Both undoped barium niobate and BCN did not show any significant conductivity values. However, both Y and Fe doped compounds show an increase in conductivity with BCNY showing a maximum conductivity of 6.6 $mScm^{-1}$ at 900 °C. Incorporation of Fe seem to induce maximum conductivity and BCNF33 showed the highest value of 41.7 $mScm^{-1}$ at 900 °C. For comparison, the Mg and Fe codoped compound, BMNF33 showed only 17 $mScm^{-1}$ at this temperature indicating that the higher ionic radii of Ca may help induce higher conductivity.(12) However, the crystallographic arrangement is also different between BCNF and BMNF as the BCNF has the Fm-3m space group while BMNF is Pm3m, which could also play a role in changing the electrical properties. Further measurements utilizing BCNF as anode for EOCM application is currently underway and will be reported in future communications.

Conclusions

Doped barium niobates show very good chemical stability under harsh carbonaceous reducing conditions. Mg and Fe codoped barium niobates previously reported by us showed good methane activation properties along with chemical stability but suffered from poor electrical conductivity. Experiments with Ca and Fe codoped BCNF perovskites are seen to retain the good methane activation and chemical stability properties along with significantly enhanced electrical conductivity properties. TGA measurements indicate about 0.44, 0.525, ad 0.497% higher weight loss under 4% H_2/N_2 in comparison to measurement under air for BCNF17, BCNF25, and BCNF33 respectively possibly due to oxygen loss. The higher electrical conductivity 42 $mScm^{-1}$ obtained for BCNF33 in comparison to Mg and Fe codoped barium niobates indicate the potential role of dopants in fine tuning the electrical and catalytic properties of doped barium niobates. Further measurements are underway to establish their EOCM properties.

Acknowledgments

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