9-21-2013

Enhanced Reducibility and Conductivity of Na/K-Doped $\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3$

Guoliang Xiao

Sirikanda Nuansaeng

Lei Zhang

Suwit Suthirakun

Andreas Heyden

University of South Carolina - Columbia, heyden@cec.sc.edu

See next page for additional authors

Follow this and additional works at: https://scholarcommons.sc.edu/emec_facpub

Part of the [Applied Mechanics Commons](#), [Materials Science and Engineering Commons](#), and the [Other Mechanical Engineering Commons](#)

Publication Info

Published in *Journal of Materials Chemistry A*, Volume 1, Issue 35, 2013, pages 10546-10552.

©Journal of Materials Chemistry A 2013, Royal Society of Chemistry.

This article cannot be redistributed or further made available.

This article was first published by the Royal Society of Chemistry and can be found at <http://dx.doi.org/10.1039/C3TA11631J>

Xiao, G., Nuansaeng, S., Zhang, L., Suthirakun, S., Heyden, A., zur Loye, H.-C., & Chen, F. (21 September 2013). Enhanced Reducibility and Conductivity of Na/K-Doped $\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3$. *Journal of Materials Chemistry A*, 1 (35), 10546 – 10552. <http://dx.doi.org/10.1039/C3TA11631J>

This Article is brought to you by the Mechanical Engineering, Department of at Scholar Commons. It has been accepted for inclusion in Faculty Publications by an authorized administrator of Scholar Commons. For more information, please contact digres@mailbox.sc.edu.

Author(s)

Guoliang Xiao, Sirikanda Nuansaeng, Lei Zhang, Suwit Suthirakun, Andreas Heyden, Hans-Conrad zur Loye, and Fanglin Chen

Enhanced reducibility and conductivity of Na/K-doped
 $\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3$ Cite this: *J. Mater. Chem. A*, 2013, **1**, 10546Guoliang Xiao,^a Sirikanda Nuansaeng,^a Lei Zhang,^a Suwit Suthirakun,^b Andreas Heyden,^b Hans-Conrad zur Loye^c and Fanglin Chen^{*a}

Donor and acceptor co-doped SrTiO_3 materials have shown interesting features in their conductivity and reducibility. In this work, 10 mol% Na^+ or K^+ as acceptor dopants have been introduced into the A-site of donor-doped strontium titanate, $\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3$, and the doping impact on their properties has been studied. By doping with Na or K, the sinterability of $\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3$ in reducing atmospheres has been improved. $\text{Na}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ and $\text{K}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ show metallic conduction behavior after being sintered at 1400 °C in 5% H_2/N_2 . Electrical conductivity reaches 1180 S cm^{-1} at 400 °C and 272 S cm^{-1} at 800 °C for $\text{K}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$, which is higher than that of $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ prepared under similar conditions, indicating the improved reducibility of acceptor doped $\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3$. Such improvement may be attributed to the improved oxide ionic conductivity and cation mobility at high temperatures. Reduced polarization resistance is also observed using $\text{Na}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ and $\text{K}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ as anodes on YSZ electrolytes, suggesting improved catalytic activity by Na/K-doping.

Received 24th April 2013

Accepted 9th July 2013

DOI: 10.1039/c3ta11631j

www.rsc.org/MaterialsA

1 Introduction

Mixed ionic and electronic conductors (MIECs) have been studied intensively due to their unique capability to conduct both electronic charge carriers (electrons, holes) and various ions (O^{2-} , Li^+ , Ag^+ , etc.) in various applications such as batteries, fuel cells, sensors and separation membranes.¹ MIECs conducting oxide ions have been considered as important cathode candidates for solid oxide fuel cells (SOFCs) because their mixed oxide ionic and electronic conduction is expected to extend the electrode reaction zone from the electrolyte/electrode interfaces potentially to the entire electrode surface. Significant reduction in polarization losses with the MIEC cathode has been reported extensively.^{2,3} Recently, in order to improve the durability of SOFCs when operating on practical fuels such as natural gas, coal-derived syngas, and biomass gas, numerous MIECs have been investigated as anodes due to their lower affinity to sulfur and higher coking resistance.^{4,5} Among the well-studied ceramic anode candidates, SrTiO_3 -based materials represent an important family.

Donor-doped SrTiO_3 materials have shown impressively high n-type electronic conductivity under anodic conditions. For those doped on the A-site, $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ reported by Marina *et al.* has exhibited an initial conductivity of $80\text{--}360 \text{ S cm}^{-1}$ at

1000 °C in a reducing environment and $\text{Sr}_{0.86}\text{Y}_{0.08}\text{TiO}_3$ reported by Hui *et al.* has also shown a high conductivity of 82 S cm^{-1} at 800 °C under similar testing conditions.^{6,7} Furthermore, upon doping Nb^{5+} on the B-site, the electrical conductivity of $\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ has been reported to reach 340 S cm^{-1} at 800 °C at low Po_2 .⁸ However, donor-doped SrTiO_3 materials may not always show high conductivity due to different charge compensation mechanisms at different Po_2 .^{9,10} Under oxidizing conditions, excess charge from the donor dopants may be compensated by strontium vacancies. In the case of Nb-doped SrTiO_3 , SrO-rich phases have been observed in samples synthesized in air.¹¹ In order to make electronic compensation dominant and increase conductivity, donor-doped SrTiO_3 materials typically need to be equilibrated at low Po_2 . Such an equilibration process involves diffusion of both Sr^{2+} and O^{2-} . Sr^{2+} diffusion is known to be extremely slow below the sintering temperature. Although diffusion of oxide ions is much faster compared with the metal cations, it is still much lower in the donor doped SrTiO_3 than in the acceptor doped or un-doped SrTiO_3 due to the suppression of oxygen vacancies by the donor dopant.⁹ Such slow kinetics of the donor doped SrTiO_3 materials also results in a slow equilibrium process at different Po_2 . Consequently, different conductivity values have been reported depending on the material processing history. Therefore, by enhancing the oxide ion conductivity of the donor doped SrTiO_3 , an accelerated equilibrium process and higher electrical conductivity during reduction can be expected.

Acceptor doping on the B-site of SrTiO_3 has been found to be an effective way to improve the oxygen ionic conductivity of the donor doped SrTiO_3 . Li *et al.* have reported improved oxide

^aDepartment of Mechanical Engineering, University of South Carolina, Columbia, South Carolina 29208, USA. E-mail: chenfa@cec.sc.edu; Tel: +1 803 777 4875^bDepartment of Chemical Engineering, University of South Carolina, Columbia, South Carolina 29208, USA^cDepartment of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, USA

ionic conductivity in La and Co/Sc co-doped SrTiO_3 .^{12,13} In our previous report, B-site doping of Ga in $\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ has demonstrated improved reducibility, and higher conductivity was obtained with $\text{Sr}_{0.9}\text{Ti}_{0.7}\text{Ga}_{0.1}\text{Nb}_{0.2}\text{O}_3$ upon reduction.¹⁴ Neagu and Irvine systematically studied the oxygen stoichiometry and conduction behavior of $\text{La}_{0.4}\text{Sr}_{0.4}\text{Ti}_{1-x}\text{Ga}_x\text{O}_3$ and similar results have also been observed.¹⁵ Due to the increase in oxygen vacancies and flexible oxygen coordination of Ga^{3+} , the materials with optimized composition have shown higher conductivity after being reduced under similar conditions. These experimental observations have also been supported by our recent computational calculations.^{16,17}

In order to test the hypothesis that the acceptor-doping is a general approach to improve the electrical property of donor-doped SrTiO_3 , in this study, we have adopted another approach to dope suitable acceptor dopants on the A-site of 20% Nb-doped SrTiO_3 . Since the valence state of Sr is only +2 in SrTiO_3 , acceptor dopants on the A-site can only be alkali metal cations. Na^+ and K^+ have comparable ionic radii to Sr^{2+} and Hou *et al.* demonstrated that the substitution of K for Sr in SrFeO_3 -based perovskite maximizes Fe–O–Fe interactions by stabilization of the untilted structure and promotes ionic conductivity at high temperatures.¹⁸ Therefore, 10% of strontium in 20% Nb-doped SrTiO_3 is substituted by Na^+/K^+ in this study. The impact of acceptor-doping on the crystalline phase, electrical conductivity and electrochemical performance of $\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3$ has been systematically studied.

2 Experimental

2.1 Sample preparation

$\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$, $\text{Na}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ and $\text{K}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ samples were synthesized by solid state reactions starting from SrCO_3 (99%), TiO_2 (99.9%), Nb_2O_5 (99.9%), Na_2CO_3 (99%) and CH_3COOK (99%). The chemicals were weighed according to the stoichiometry and mixed in a mortar with ethanol as medium. After being dried, the mixed powder was calcined at 900 °C for 6 h in air. The powder was then ground, pressed into pellets and calcined at 1250 °C in air for 20 h. This calcination step was repeated another time to improve phase purity. The obtained powder was finally pressed into bars (about $35 \times 5 \times 1 \text{ mm}^3$ after sintering) and pellets and sintered for 10 h in air or 5% H_2 (balanced with N_2) at 1400 or 1500 °C. Poly-vinyl-butyril (PVB, 1.5 wt%) was used as a binder. The P_{O_2} of the 5% H_2/N_2 used in this work was monitored using an oxygen sensor at 800 °C and the value was about 10^{-22} bar. All the sintered samples exhibited high relative density (above 95%) except for the $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ bar sample sintered in 5% H_2/N_2 at 1400 °C, which has a relative density of about 85%. A muffle furnace (MTI KSL1700X) was used for high temperature treatment in air and a tubular furnace (MTI GSL1700S) was used for high temperature reduction in this work.

2.2 Characterization

The phase purity of the samples was examined by X-ray diffraction (XRD) at $20^\circ \leq 2\theta \leq 80^\circ$ conducted on a D/MAX-3C

X-ray diffractometer equipped with a graphite monochromator and Cu $K\alpha$ radiation. The lattice parameters were calculated using Jade software. The density of the sintered samples was tested by the Archimedes method. The morphology of the samples was characterized using a scanning electron microscope (SEM, FEI Quanta and XL 30) and elemental analysis of the samples was carried out using a SEM equipped with an energy dispersive X-ray spectrometer (EDX).

2.3 Electrical and electrochemical evaluation

The conductivity of the samples in air was tested on pellets with diameters around 11 mm and thickness about 1 mm after sintering. Pt paste (Heraeus CL11-5100) was used as the current collector and fired at 1000 °C for 0.5 h prior to the conductivity test. Rectangular bar samples were used for reducibility and conductivity measurements by a standard dc four-probe method. Silver conducting paste was used to assemble the silver lead wires on bar samples. The resistance of the samples was recorded using a multimeter (Keithley model 2001 7-1/2 DDM). For reducibility measurements, the bar samples were sintered in air at 1400 °C and equilibrated at 800 °C in N_2 (80 ml min^{-1} , $P_{\text{O}_2} \sim 10^{-5}$ bar at 800 °C) for 20 h. Then, the gas was switched to H_2 (80 ml min^{-1} , $P_{\text{O}_2} \sim 10^{-26}$ bar at 800 °C) and resistance variation with time was recorded.

The polarization resistance was tested on symmetric cells supported by a YSZ (8YSZ, Tosh) electrolyte. YSZ pellets were sintered at 1550 °C (diameter about 11 mm, thickness about 1 mm). Electrode slurry was made by mixing the sample powder with a binder (Heraeus V006) at a weight ratio of 1 : 1.5. Symmetric cells were fabricated by painting the electrode slurry on both sides of YSZ pellets and fired at 1300 °C in 5% H_2/N_2 . Pt paste was used as the current collector and fired at 1000 °C for 0.5 h in 5% H_2/N_2 . The impedance spectra of the symmetric cells were recorded in H_2 (3 vol% H_2O) using an electrochemistry workstation (IM6-Zahner).

3 Results and discussion

3.1 Phase development

A nonstoichiometric effect study in Y-doped SrTiO_3 has shown a dramatic, negative influence of excess Sr content on the conductivity.¹⁹ In this work, slight Sr-deficiency was adopted in $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ to prevent the number of A-site cations from being larger than that of the B-site cations (*i.e.*, $\text{Sr}/(\text{Ti} + \text{Nb}) > 1$). XRD patterns of the powders synthesized at 1250 °C in air are shown in Fig. 1. According to the electro-neutrality condition, the extra charge of Nb^{5+} (Nb_{Ti} in the Nb-doped SrTiO_3) needs to be compensated. Under oxidizing atmospheres, it cannot be balanced by reducing Ti^{4+} to Ti^{3+} (Ti_{Ti}) or forming interstitial oxygen (O_i) in the perovskite lattice at intermediate temperatures (below the sintering temperature). Several reports suggested that strontium vacancies will form to compensate the extra charge from Nb and Sr-rich secondary phases can be observed. As shown in Fig. 1, besides the cubic perovskite phase some impurity peaks were observed in the pattern of $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ where the impurity peaks probably belong to

Fig. 1 XRD patterns of powders after solid state reactions at 1250 °C in air (Δ denotes peaks from the perovskite phase; * denotes the peaks from the impurity phase $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ (JCPDS 48-0421)).

the phase of $\text{Sr}_5\text{Nb}_4\text{O}_{15}$ (JCPDS 48-0421). In Na^+ or K^+ doped samples, the extra charge of Nb^{5+} can be partially balanced by Na'_{Sr} or K'_{Sr} . Consequently, less impurity peaks are shown for these two samples in Fig. 1.

As oxygen partial pressure decreases, the extra charge from the donor dopant starts to be compensated electronically by reduction of Ti^{4+} to Ti^{3+} (Ti'_{Ti}). The Sr-rich secondary phases will combine with the Sr vacancies formed under oxidizing conditions and finally the stoichiometric compositions will form. As shown in Fig. 2, a cubic perovskite phase was obtained after sintering the samples at 1400 °C in 5% H_2/N_2 . The XRD patterns obtained from the samples sintered in air are also shown in Fig. 2. Raising the sintering temperature accelerates diffusion of cations and further improves the homogeneity of the samples. The impurity peaks even become undetectable after $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ being sintered at 1400 °C in air. Similar results have also been reported by Gross *et al.*²⁰ Constraint thermodynamic calculations have shown that the

Fig. 2 XRD patterns of samples after sintering at 1400 °C in air or 5% H_2/N_2 .

stoichiometric phase is thermodynamically stable at high temperatures even in oxidizing atmospheres due to the release of the lattice oxygen.¹⁶ Therefore, the phase purity may be improved during sintering. When the sample is being exposed to a lower temperature than that in the sintering process, the Sr-enriched phase tends to precipitate out but the sample may still retain the stoichiometric phase due to the extremely slow cation and oxide ion mobility of Nb-doped SrTiO_3 at low temperatures.

Lattice parameters of the samples sintered at 1400 °C in different atmospheres are summarized in Table 1. Since Sr^{2+} (158 pm) is larger than Na^+ (153 pm) and smaller than K^+ (178 pm),²¹ the lattice parameter of $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ is expected to increase with K^+ doping and decrease with Na^+ doping according to Vegard's law.²² As expected, the lattice parameter of the Na doped sample sintered at 1400 °C in air is smaller than those of the other two samples under the same conditions. However, the lattice parameter of the K doped sample is similar to that of the $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ sample. Considering the low melting point of sodium and potassium oxides, evaporation of Na or K may occur during the high temperature sintering process. Consequently, one possible explanation for the smaller lattice parameter of $\text{K}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ than what is expected from Vegard's law may be the loss of K content during sintering. This will also lead to a slight A-site deficiency in $\text{K}_x\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ ($x = 0.063$ according to elemental analysis). The lattice shrinkage in Sr-deficient Nb-doped SrTiO_3 was also reported by Blennow *et al.*¹¹

All samples showed expansion in the lattice parameter after reduction as listed in Table 1. According to the defect chemistry of the donor doped SrTiO_3 , the compensation mechanism of the extra charge of the donor dopant in reducing atmospheres is quite different from that in the oxidizing atmospheres, which has been well discussed in Y-doped SrTiO_3 by Fu *et al.*⁹ In the case of Nb-doped SrTiO_3 , the extra charge of Nb'_{Ti} will be compensated electronically by formation of Ti'_{Ti} under moderately reducing conditions and donor type $\text{V}_\text{O}^\bullet$ will be generated due to further reduction of Ti^{4+} to Ti^{3+} under highly reducing conditions. Such electronic compensations may result in large expansion in the lattice. Particularly, Na or K doped $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ showed even larger lattice parameters than the $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ sample, implying that higher concentration of charge carriers, Ti^{3+} , may be formed in $\text{Na}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ or $\text{K}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ samples sintered at 1400 °C under reducing conditions.

3.2 Microstructure and elemental analysis

SEM images of the bar samples sintered at 1400 °C in 5% H_2/N_2 are shown in Fig. 3. It can be clearly seen that $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ shows low sinterability under the given conditions while the alkali metal ion doped samples look rather dense with larger particle size. This is consistent with the density of the bar samples obtained by the Archimedes method. The relative density of $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ only achieved 85% while that of $\text{Na}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ or $\text{K}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ is above 95%. The low sinterability of donor doped SrTiO_3 has also been reported in stoichiometric La, Y-doped SrTiO_3 ,^{9,21} probably due to low

Table 1 Lattice parameters of the samples (s.g. $Pm3m$) sintered at 1400 °C in air (oxidizing) or 5% H_2/N_2 (reducing) atmospheres

		$Sr_{0.99}Ti_{0.8}Nb_{0.2}O_3$	$Na_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$	$K_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$
Lattice parameter ($\text{\AA} \pm 0.001$)	Oxidizing	3.9219(3)	3.9164(3)	3.9213(6)
	Reducing	3.9273(6)	3.9295(3)	3.9305(4)

Fig. 3 SEM images captured from the fracture surface of (a) $Sr_{0.99}Ti_{0.8}Nb_{0.2}O_3$, (b) $Na_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$, and (c) $K_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$ bar samples sintered at 1400 °C in 5% H_2/N_2 and EDX spectra of (d) $Na_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$, and (e) $K_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$.

cation mobility in these compositions. Considering the low melting point of alkali metal oxides, doping with Na^+/K^+ may aid the sintering process of donor doped $SrTiO_3$.

The Na and K contents in the sintered bar samples were investigated by EDX. As the spectra show in Fig. 3d and e, sodium and potassium signals have been clearly detected. Further quantitative elemental analysis showed that the atomic ratio of alkali metal to strontium was about 1 : 13 and 1 : 15 for the Na and K doped samples, respectively. The ratios are slightly lower than the nominal ratio of 1 : 9 in the doped samples. The elemental analysis result is in agreement with the lattice shrinkage observed from the XRD analysis. Therefore, the loss of alkali metal ions during the high temperature sintering process results in slight A-site deficiency in the materials. Sr-deficiency has been demonstrated to have positive effects on sintering in different donor doped $SrTiO_3$.²¹ This may be another reason for the higher density achieved by Na and K doped samples sintered at 1400 °C in 5% H_2/N_2 .

3.3 Electrical conductivity

Electrical conductivity in air is measured for samples sintered at 1400 °C in air and the results are shown in Fig. 4. The donor dopant introduces extra lattice oxygen into the material and makes the presence of oxygen vacancies unlikely in oxidizing

atmospheres. $Sr_{0.99}Ti_{0.8}Nb_{0.2}O_3$ shows relatively low electrical conductivity in air due to lack of either electronic charge carriers (Ti_{Ti}') or ionic charge carriers ($V_O^{\bullet\bullet}$). Introducing acceptor dopants such as Na^+ and K^+ to the A-site is expected to mitigate the depression of oxygen vacancies by the donor dopant Nb^{5+} . As shown in Fig. 4, $Na_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$ and

Fig. 4 Electrical conductivity in air measured for samples sintered in air at 1400 °C.

Fig. 5 Electrical conductivity in H_2 measured for samples sintered (a) at 1400 °C and (b) 1500 °C in 5% H_2/N_2 .

$K_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$ demonstrated improved conductivity in air. Furthermore, the electrical conductivity of $K_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$ was one order of magnitude higher than that of $Sr_{0.99}Ti_{0.8}Nb_{0.2}O_3$ in air. Li *et al.* also reported that either A-site-deficiency or acceptor doping will improve the ionic conductivity of donor-doped $SrTiO_3$ by introducing more oxygen vacancies.^{23,24}

Fig. 5a shows the electrical conductivity measured between 400 °C and 800 °C in H_2 for bar samples sintered at 1400 °C in 5% H_2/N_2 . For each point, the data were recorded after holding the sample at the temperature for 2 h. Generally, the electrical conductivity of the three samples is high and above 100 S cm^{-1} at all the tested temperatures, indicating that electronic compensation occurred in the samples after reduction. The electrical conductivity of $Sr_{0.99}Ti_{0.8}Nb_{0.2}O_3$ was between 150 and 203 S cm^{-1} and it is almost independent of temperature. Similar results were also reported by Gross *et al.* for the same composition.²⁰ Since metallic behavior is expected for electronically compensated $Sr_{0.99}Ti_{0.8}Nb_{0.2}O_3$, such conduction behavior indicates the nonequilibrium state of the sample. The conductivity of $Sr_{0.99}Ti_{0.8}Nb_{0.2}O_3$ only slightly surpasses the conductivity measured for $Na_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$ at 800 °C but is still lower than the conductivity measured for $K_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$ at all testing temperatures. The conductivity of $K_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$ ranged from 1180 S cm^{-1} at 400 °C to 272 S cm^{-1} at 800 °C and that of $Na_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$ ranged from 340 S cm^{-1} at 400 °C to 151 S cm^{-1} at 800 °C. Both $K_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$ and $Na_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$ showed metallic type electrical conduction behavior. The conductivity results shown in Fig. 5a suggest that Na or K doping accelerates the charge compensation process of $Sr_{0.99}Ti_{0.8}Nb_{0.2}O_3$ in reducing atmospheres. Such improvement can be probably attributed to the higher mobility of Na^+ or K^+ during sintering and the improved oxide ion conductivity at high temperatures.

Fig. 5b shows the electrical conductivity measured for bar samples sintered at 1500 °C in 5% H_2/N_2 . As sintering temperature increased, the relative density of the $Sr_{0.99}Ti_{0.8}Nb_{0.2}O_3$ bar sample increased to above 95%. Due to further reduction at higher temperature, the conductivity of $Sr_{0.99}Ti_{0.8}Nb_{0.2}O_3$ samples increased dramatically with the value ranging from 2319 S cm^{-1} at 400 °C to 508 S cm^{-1} at 800 °C and a metallic

Fig. 6 Electrical conductivity variation with time after switching the gas from N_2 to H_2 at 800 °C.

behavior was observed, indicating that the samples sintered at higher temperature more closely approach the equilibrium state in reducing atmospheres. The conductivity of $K_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$ and $Na_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$ did not change significantly, suggesting that the alkali metal doped samples are more easily equilibrated at lower temperatures. The conductivity of $K_{0.1}Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$ even dropped slightly after raising the sintering temperature to 1500 °C which may be attributed to the further loss of K content. The improvement in reducibility in Na or K doped $Sr_{0.99}Ti_{0.8}Nb_{0.2}O_3$ was further confirmed by recording electrical conductivity variation as a function of time

Fig. 7 Polarization resistance measured at 850 °C in wet H_2 measured on symmetric cells.

Fig. 8 SEM images of (a) $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$, (b) $\text{Na}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$, and (c) $\text{K}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ electrodes fired at 1300 °C in 5% H_2/N_2 for 2 h.

of the bar samples sintered in air after switching the sample environment from N_2 to H_2 at 800 °C and the results are shown in Fig. 6. The samples were all well sintered and their relative densities were all about 95% such that the impact of microstructure can be neglected. Generally, the conductivities of the samples are higher than those measured in air but still much lower than those measured for samples sintered in reducing atmospheres. $\text{Na}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ and $\text{K}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ exhibited relatively higher conductivity upon reduction for a short period. Within 10 h, the electrical conductivity of $\text{Na}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ and $\text{K}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ increased to above 1 S cm^{-1} while that of $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ was still less than 0.6 S cm^{-1} .

3.4 Polarization resistance under anodic conditions

The donor doping effect on the anode performance of $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ was studied in symmetric cells. Impedance spectra of the electrodes fabricated on YSZ pellets were tested in wet H_2 (3 vol% H_2O). Fig. 7 shows the Nyquist plots recorded at 850 °C for $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$, $\text{Na}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ and $\text{K}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ electrodes fired at 1300 °C in 5% H_2/N_2 for 2 h. Depressed arcs can be observed which represent the H_2 -oxidation processes in the electrodes. Ohmic resistance from the electrolyte, electrodes and lead wires determined by the first intersection of the arc and x-axis was removed from the spectra for a clear comparison. The difference between the two intersections of the arcs is the polarization resistance which is determined by the contributions from the charge transfer process, adsorption and dissociation of H_2 , and desorption of H_2O . As shown in Fig. 7, the polarization resistance of Na and K doped samples is evidently smaller than that of $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$. This can be presumably attributed to the higher oxygen vacancy concentration in the Na or K-doped samples which benefits the charge transfer process by improving the oxide ionic conductivity in reducing atmospheres. It can be still observed in Fig. 7 that the high frequency impedance of $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ significantly decreased after doping with Na/K and the corresponding sum frequencies of the arcs for Na and K doped $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ were only about 7.4 Hz, confirming that the charge transfer process was facilitated. Blennow *et al.* observed the low frequency impedance response for $\text{Sr}_{0.94}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3$ changing with H_2 partial pressure and ascribed it to H_2 adsorption/desorption.²⁵ Therefore, the lower frequency response of $\text{Na}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ and $\text{K}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ indicates that their performance can be further improved by optimizing the electrode microstructure. Fig. 8 shows SEM images taken on cross-sections of the tested

cells. Larger particles can be observed in the $\text{Na}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ and $\text{K}_{0.1}\text{Sr}_{0.9}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ electrodes than those in the $\text{Sr}_{0.99}\text{Ti}_{0.8}\text{Nb}_{0.2}\text{O}_3$ electrode prepared under similar conditions, suggesting that Na and K doped samples were slightly over sintered, indicating that the alkali metal doping may improve sinterability of Nb-doped SrTiO_3 . It may also be the cause for the lower frequency response of Na/K-doped samples shown in Fig. 7. The polarization resistance is still too large for Nb-doped SrTiO_3 materials due to their generally low ionic conductivity. By applying these materials in the composite electrodes, the polarization resistance can be dramatically decreased.²⁵

4 Conclusions

Enhanced electrical conductivity has been observed in Na or K doped $\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3$ sintered at lower temperatures. Due to either the low melting point of Na and K oxides or a slight A-site deficiency of the sintered samples, Na or K doped $\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3$ exhibited improved sinterability. The substitution of Sr^{2+} by Na^+ or K^+ improves the equilibration kinetics of Nb-doped SrTiO_3 in reducing atmospheres and the electrochemical activity for H_2 oxidation when used as an SOFC anode material.

Acknowledgements

This work was supported as part of the HeteroFoaM Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0001061.

References

- 1 I. Riess, *Solid State Ionics*, 2003, **157**, 1.
- 2 Z. Shao and S. M. Haile, *Nature*, 2004, **431**, 170.
- 3 X. Xu, C. Xia, G. Xiao and D. Peng, *Solid State Ionics*, 2005, **176**, 1513.
- 4 P. I. Cowin, C. T. G. Petit, R. Lan, J. T. S. Irvine and S. Tao, *Adv. Energy Mater.*, 2011, **1**, 314.
- 5 J. B. Goodenough and Y. Huang, *J. Power Sources*, 2007, **173**, 1.
- 6 O. A. Marina, N. L. Canfield and J. W. Stevenson, *Solid State Ionics*, 2002, **149**, 21.
- 7 S. Hui and A. Petric, *J. Eur. Ceram. Soc.*, 2002, **22**, 1673.
- 8 T. Kolodiaznyh and A. Petric, *J. Electroceram.*, 2005, **15**, 5.
- 9 Q. Fu, S. Mi, E. Wessel and F. Tietz, *J. Eur. Ceram. Soc.*, 2008, **28**, 811.

- 10 Q. Fu, F. Tietz and D. Stover, *J. Electrochem. Soc.*, 2006, **153**, D74.
- 11 P. Blennow, A. Hagen, K. K. Hansen, L. R. Wallenberg and M. Mogensen, *Solid State Ionics*, 2008, **179**, 2047.
- 12 X. Li, H. Zhao, F. Gao, N. Chen and N. Xu, *Electrochem. Commun.*, 2008, **10**, 1567.
- 13 X. Li, H. Zhao, N. Xu, X. Zhou, C. Zhang and N. Chen, *Int. J. Hydrogen Energy*, 2009, **34**, 6407.
- 14 G. Xiao, X. Dong, K. Huang and F. Chen, *Mater. Res. Bull.*, 2011, **46**, 57.
- 15 D. Neagu and J. T. S. Irvine, *Chem. Mater.*, 2011, **23**, 1607.
- 16 S. Suthirakun, S. C. Ammal, G. Xiao, F. Chen, H. C. zur Loye and A. Heyden, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **84**, 205102.
- 17 S. Suthirakun, S. C. Ammal, G. Xiao, F. Chen, K. Huang, H. C. zur Loye and A. Heyden, *Solid State Ionics*, 2012, **228**, 37.
- 18 S. Hou, J. A. Alonso and J. B. Goodenough, *J. Power Sources*, 2010, **195**, 280.
- 19 Q. Ma, F. Tietz and D. Stover, *Solid State Ionics*, 2011, **192**, 535.
- 20 M. D. Gross, K. M. Carver, M. A. Deighan, A. Schenkel, B. M. Smith and A. Z. Yee, *J. Electrochem. Soc.*, 2009, **156**, B540.
- 21 R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.*, 1976, **32**, 751.
- 22 A. R. Denton and N. W. Ashcroft, *Phys. Rev. A*, 1991, **43**, 3161.
- 23 X. Li, H. Zhao, X. Zhou, N. Xu, Z. Xie and N. Chen, *Int. J. Hydrogen Energy*, 2010, **35**, 7913.
- 24 X. Li, H. Zhao, F. Gao, Z. Zhu, N. Chen and W. Shen, *Solid State Ionics*, 2008, **179**, 1588.
- 25 P. Blennow, K. K. Hansen, L. R. Wallenberg and M. Mogensen, *Solid State Ionics*, 2009, **180**, 63.