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Sr_{3-3x}Na_{3x}Si₃O_{9-1.5x} (x = 0.45) As a Superior Solid Oxide-Ion Electrolyte for Intermediate Temperature-Solid Oxide Fuel Cells

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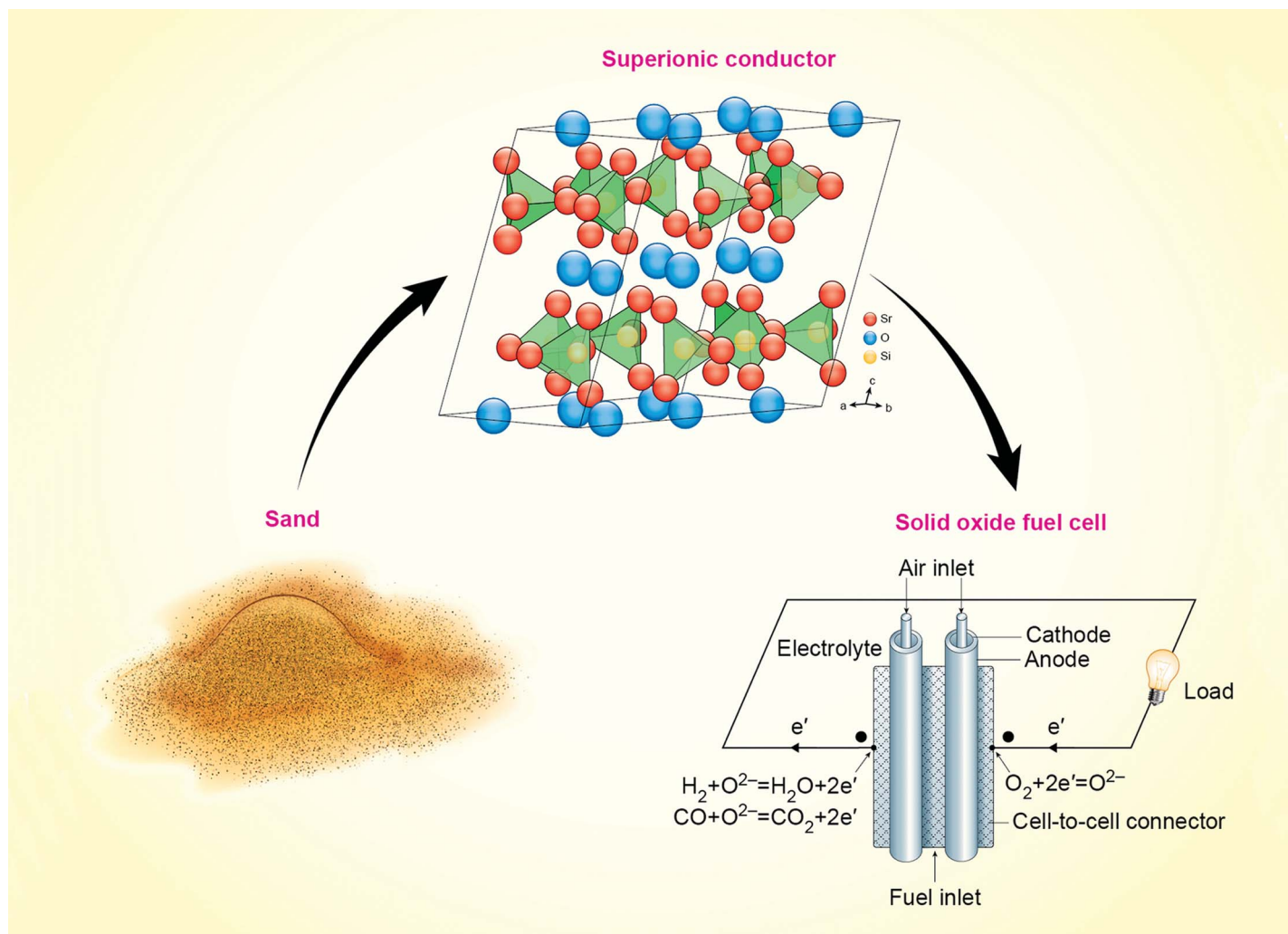
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Showcasing research from Kevin Huang's Laboratory,
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Carolina, Columbia, USA.

Title: $Sr_{3-3x}Na_{3x}Si_3O_{9-1.5x}$ ($x = 0.45$) as a superior solid oxide-ion
electrolyte for intermediate temperature-solid oxide fuel cells

The paper highlights the discovery of a new solid-state oxide-ion
conductor using low cost and rare-earth free materials. Its
conductivity is the highest among all the known oxide-ion
conductors, purely ionic and chemically stable from oxidizing
to reducing atmospheres. It exhibits great potential to be a new
class of technologically and strategically important materials for
commercial solid state ionic devices including solid oxide fuel
cells, electrolyzers, sensors and separation membranes.

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$\text{Sr}_{3-3x}\text{Na}_{3x}\text{Si}_3\text{O}_{9-1.5x}$ ($x = 0.45$) as a superior solid oxide-ion electrolyte for intermediate temperature-solid oxide fuel cells

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We here report that a newly discovered superior oxide-ion conductor $\text{Sr}_{3-3x}\text{Na}_{3x}\text{Si}_3\text{O}_{9-1.5x}$ ($x = 0.45$) (SNS) demonstrates full potential to be a practical solid electrolyte for intermediate temperature-solid oxide fuel cells (IT-SOFCs). It exhibits the highest oxide-ion conductivity with the lowest activation energy among all the chemically stable solid oxide-ion conductors reported. The ionic conductivity is stable over a broad range of partial pressures of oxygen (10^{-30} to 1 atm) for an extended period of time. A SOFC based on a 294 μm thick SNS-electrolyte produces peak power densities of 431 and 213 mW cm^{-2} at 600 and 500 $^{\circ}\text{C}$, respectively. Considering its competitive costs in materials and manufacturing and rare-earth free composition, SNS has great potential to become a new class of technologically and strategically important electrolytes for commercial IT-SOFCs.

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Broader context

Compared to the conventional internal combustion engines, a high-temperature solid oxide fuel cell (SOFC) can offer a doubling of the chemical-to-electrical efficiency and therefore emits half of the greenhouse gas per unit electricity produced. However, the commercialization of SOFC technology is hampered by high cost and poor reliability, which are all linked to severe material challenges resulting from the high-temperature operation. Reducing the operating temperature to an intermediate temperature (IT) range, *viz.* 200–500 $^{\circ}\text{C}$, has great potential to significantly lower the cost and enhance the reliability of an SOFC, thus rendering it commercially viable. One of the key elements to the realization of IT-SOFCs is the oxide-ion conducting electrolyte with ionic conductivity $\geq 10^{-2}$ S cm^{-1} at <500 $^{\circ}\text{C}$. None of the existing chemically stable oxide-ion conductors can fulfill that requirement yet. The present work demonstrates that a newly discovered 2D layered oxide-ion conductor $\text{Sr}_{3-3x}\text{Na}_{3x}\text{Si}_3\text{O}_{9-1.5x}$ ($x = 0.45$) can be an ideal solid electrolyte for IT-SOFCs in light of conductivity, stability and electrochemical performance. In addition, this new electrolyte uses inexpensive, rare-earth free materials and can be easily fabricated at relatively lower temperatures with low manufacturing cost. All of these advantages have promised the new electrolyte to be a new class of technologically and strategically important materials for commercial IT-SOFCs.

Introduction

Over the past half a century, clean and efficient solid oxide fuel cell (SOFC) technology has been developed to the stage that a further reduction in operating temperature from the current ≥ 800 $^{\circ}\text{C}$ to ≤ 600 $^{\circ}\text{C}$ is necessary in order for it to commercially compete with internal combustion engines.^{1,2} Fast oxide-ion conductors are key functional components determining the operating temperature of a solid oxide fuel cell. With the existing oxide-ion conductor systems such as Y_2O_3 -stabilized ZrO_2 , Gd_2O_3 -doped CeO_2 and Sr- and Mg-doped LaGaO_3 , it would seem to be very difficult to achieve such reduced-temperature SOFCs at a commercial scale.

It is very interesting to note that all the existing oxide-ion conductors possess one of the following crystal structures: fluorite, perovskite and apatite.^{3–11} Recently, a new family of superior solid oxide-ion conductors with a 2D layered structure and a generic formula of $\text{Sr}_{3-3x}\text{A}_{3x}\text{Si}_3\text{O}_{9-1.5(x+y)}$ ($\text{A} = \text{Na}$ and K) has been identified as a promising electrolyte for intermediate temperature-solid oxide fuel cells (IT-SOFCs).^{12,13} Since Si^{4+} has a strong tetrahedral site preference, $\text{Sr}_3\text{Si}_3\text{O}_9$ does not crystallize in the perovskite structure. Instead, it forms a layered (SrSiO_3)₃ structure containing close-packed planes of Sr^{2+} in trigonal-prismatic coordination separated by a layer of Si_3O_9 units containing three SiO_4 tetrahedra sharing corners in a triangular plane of oxygen parallel to the Sr^{2+} planes.¹² The apical oxide ions of the tetrahedra coordinate to the Sr^{2+} and have close access to oxygen sites on neighboring Si_3O_9 complexes. Substitution of K^+ or Na^+ for Sr^{2+} introduces mobile oxygen vacancies,^{12,13} and steric constraints prevent the vacancies from being eliminated by a corner sharing Si_3O_9 unit. $\text{Sr}_{3-3x}\text{K}_{3x}\text{Si}_3\text{O}_{9-1.5x}$ is hygroscopic while $\text{Sr}_{3-3x}\text{Na}_{3x}\text{Si}_3\text{O}_{9-1.5x}$ is

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not. A neutron-diffraction study at different temperatures has suggested that oxygen vacancies are retained by the steric hindrance with substitution of either K^+ or Na^+ for Sr^{2+} ; ¹⁴ the vacancies occupy primarily M_3O_9 ($M = Si$ and Ge) complexes at lower temperatures with increasing apical-site occupancy as the temperature is raised. An ongoing research in authors' groups is focused on understanding the dynamics of fast oxygen transport in the new electrolyte material using the *in situ* solid-state NMR technique.

The best oxide-ion conductivity of the $Sr_{3-3x}A_{3x}Si_{3-3y}Ge_{3y}O_{9-1.5(x+y)}$ ($A = Na$ and K) series is found in the composition $Sr_{3-3x}Na_{3x}Si_3O_{9-1.5x}$ ($x = 0.45$) (herein referred to as SNS). At 500 °C, the measured oxide-ion conductivity is $>10^{-2} \text{ S cm}^{-1}$, which is equivalent to that of $La_{0.80}Sr_{0.20}Ga_{0.83}Mg_{0.17}O_{3-\delta}$ (LSGM) at 600 °C (ref. 15–17) and of $Zr_{0.92}Y_{0.08}O_{2-\delta}$ (YSZ) at 670 °C.¹⁸ It has also been reported that SNS is chemically stable in reducing atmospheres and compatible with commonly used SOFC cathodes.^{12,13} Therefore, use of SNS as a functional electrolyte in a SOFC is expected to appreciably reduce the operating temperature of the latter and finds its utility in commercial IT-SOFCs. However, until now, this promise has not yet been fully demonstrated in SOFCs. In this study, we report for the first time the characteristics of SNS as a truly functional electrolyte in a SOFC and the electrochemical performance of a SNS-based SOFC operated at 500–600 °C.

Experimental section

Synthesis and characterization of the SNS electrolyte

The SNS samples were synthesized through a two-step solid-state reaction route. The starting materials of $SrCO_3$ (Aldrich, 99.9%), SiO_2 (Alfa Aesar, 99.5%), and Na_2CO_3 (Fisher Scientific, 99.9%) were first intimately mixed in a stoichiometric ratio, followed by pelletizing under a static pressure of 200 MPa and calcining at 1000 °C for 20 hours. After breaking up and ball milling to submicron powders, the SNS powder was pelletized again and finally sintered at 1050 °C for another 20 hours for densification. To avoid reactions between SNS and an Al_2O_3 boat, a layer of loose $Sr_{3-3x}Na_{3x}Si_3O_{9-1.5x}$ ($x = 0.45$) powders was spread over the surface of Al_2O_3 prior to sintering.

The oxide-ion conductivity of the dense SNS pellets ($\sim 0.5 \text{ cm}$ in thickness and $\sim 1.5 \text{ cm}$ in diameter) was measured in the temperature range of 450–700 °C with a Solartron Electrochemical 1260/1287 system using the Electrochemical Impedance Spectroscopy (EIS) technique. The frequency was swept from 0.5 to 10^6 Hz with an AC stimulus of 10 mV to generate impedance spectra fully covering the grain and grain-boundary responses. Silver paste/mesh was used as the current collector for the measurement.

The phase purity of SNS after sintering and exposure to reducing atmospheres was examined by powder X-ray diffraction (PXRD) using an X-ray diffractometer (D/max-A, Rigaku, Japan) with graphite-monochromatized $CuK\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The XRD scan was performed at a rate of 5° min^{-1} from $2\theta = 20$ to 80° . The XRD patterns were further analyzed with the JADE (MDI) software to identify the phase structure and composition.

The thermal expansion of SNS was measured in flowing air from RT to 1000 °C with a Theta 1600 dilatometer. The

coefficient of thermal expansion (TEC) as a function of temperature was determined as the derivative of change in length with regard to temperature.

Electrochemical evaluation of the SNS-based cells

Two types of cells, *viz.* half-cell and full-cell, were fabricated based on a symmetrical ceramic structure of porous-SNS/dense-SNS/porous-SNS. The symmetrical half-cell configuration was intended to study the cathode polarization only, whereas the full-cell counterpart was aimed to evaluate the true electrochemical performance of a SNS-based SOFC. There were two steps involved in making each type of cell. The first step was to fabricate two symmetrical porous SNS scaffolds on two sides of a dense SNS membrane. To do so, a $\sim 30 \text{ }\mu\text{m}$ thick organic-loaded SNS layer was first screen printed on each side of the dense SNS membrane, followed by firing it at 1000 °C for 1 hour to obtain porosity in the thin SNS-coating and achieve good bonding with the dense SNS membrane. The second step was to infiltrate the respective electrode nanoparticles into the prefabricated symmetrical porous SNS scaffolds through nitrate solutions. After each infiltration step, the cell was fired at 400 °C for 1 hour to decompose nitrates into oxides. After a total of seven infiltration-decomposition steps, the infiltrated cell was finally fired at 800 °C for 1 hour to form the wanted phase. For the symmetrical half-cell cathode polarization study, a nitrate solution containing stoichiometric amounts of Sm, Sr and Co was impregnated equally into the two porous SNS scaffolds to yield two identical $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC)/SNS composite cathodes. For the fuel-cell performance evaluation, one side of the porous SNS scaffold was infiltrated with SSC to serve as the cathode and another side with Ni nanoparticles to serve as the anode. The effective surface area of cells was kept at 0.5 cm^2 . Silver paste/mesh was used as the current collector for all the electrochemical evaluations.

The electrochemical performance of thus fabricated cells was characterized using the same Solartron 1260/1287 system used for oxide-ion conductivity with a similar sweeping frequency range and stimulus AC signal. The DC functionality of the system was utilized to attain the characteristic $V-I$ and $P-I$ curves. The testing temperature was focused on intermediate temperatures ranging from 500 to 600 °C. A flow of 50 ml min^{-1} air and 30 ml min^{-1} dry H_2 was employed as the oxidant and fuel, respectively. Commercial glass (Schott AG, Standort Landshut, GM 31107) was used to seal the testing SOFC.

Microstructural evaluation of the SNS-based cells

The microstructural features of and compositional distribution across both the half-cells and single fuel-cells studied were captured and analyzed using a field emission scanning electron microscope (FESEM, Zeiss Ultra) equipped with an energy dispersive X-ray spectroscopy (EDS) analyzer, respectively.

Results and discussion

Oxide-ion conductivity

The measured oxide-ion conductivity of SNS is compared in the temperature range of 450–700 °C in Fig. 1 with other well-known

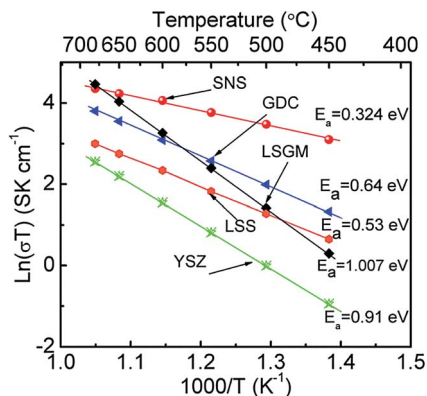


Fig. 1 Comparison of oxide-ion conductivity of SNS measured in air with other well-known oxide-ion conductors. LSGM – ref. 17; YSZ – ref. 18; GDC – ref. 19; Sr doped $\text{La}_{10}\text{Si}_6\text{O}_{27}$ (LSS) apatite – ref. 20.

chemically stable oxide-ion conductors having crystal structures of fluorite, perovskite and apatite. The Bi_2O_3 -based oxide-ion conductors are not included in the comparison for the fact that they are not chemically stable in reducing atmospheres. The exceptionally low activation energy E_a is a unique feature of SNS, making it ideal for use as an electrolyte in reduced temperature (<600 °C) SOFCs. It is believed that the easy migration of oxide-ion vacancies with a zigzag pathway in the basal plane is the origin of low activation energy observed.^{12,13} We are currently using *in situ* solid state NMR to reveal more details on the dynamics of oxide-ion transport in SNS. Due to the fact that our data were focused within a narrower temperature range than ref. 13, the curvature behavior related to defect association is not so evident in Fig. 1.

The dependence of conductivity on partial pressure of oxygen ($p\text{O}_2$) is a key indicator of pure oxide-ion conductors and electronic insulators. Fig. 2 shows the ionic conductivity measured over a $p\text{O}_2$ ranging from oxidizing pure O_2 to reducing 5% H_2 - N_2 in a temperature range of 500–650 °C. No apparent $p\text{O}_2$ -dependence of conductivity is observed over a $p\text{O}_2$ window as wide as 10^{-30} to 1 atm, suggesting that SNS is indeed a pure and chemically stable oxide-ion conductor.

The stability of oxide-ion conductivity over time is another important characteristic for a practically meaningful oxide-ion conductor. Fig. 3 shows the oxide-ion conductivity of SNS

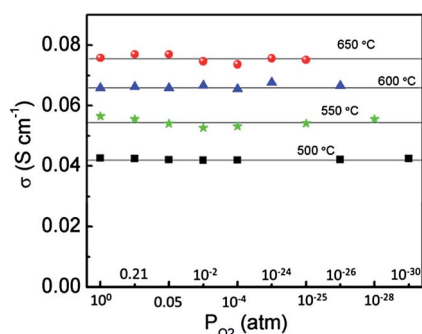


Fig. 2 Variation of oxide-ion conductivity of SNS with $p\text{O}_2$ at 500–650 °C.

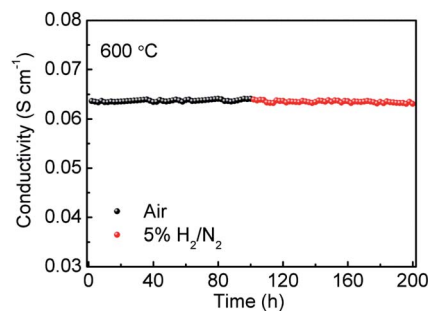


Fig. 3 Oxide-ion conductivity of SNS as a function of time measured in air and dry 5% H_2 - N_2 .

measured in two extreme atmospheres: air and 5% H_2 - N_2 , at 600 °C, over a 200-hour period. No obvious change in conductivity is observed, suggesting that the oxide-ion conducting phase in SNS is stable. This observation is consistent with Fig. 4, where XRD patterns of the sample are shown to be unchanged after the exposure to dry 5% H_2 - N_2 and even pure H_2 .

Microstructure

The dense microstructure of SNS after densification at 1050 °C is shown in Fig. 5 from the surface as well as the fracture. Compared to other commonly known oxide-ion conductor counterparts, low-temperature densification (1050 °C) for SNS implies lower manufacturing cost. This feature combined with the fact that SNS uses inexpensive and rare-earth-free constituents makes the new electrolyte an ideal, cost-competitive and strategically important solid electrolyte for commercial IT-SOFCs.

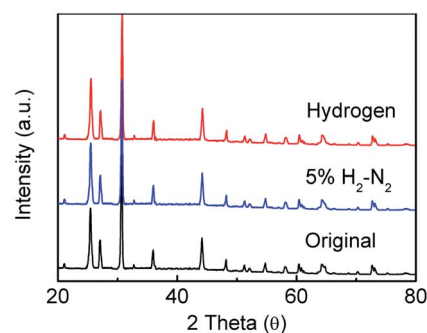


Fig. 4 Comparison of XRD patterns of SNS before and after exposure to 5% H_2 - N_2 and pure hydrogen.

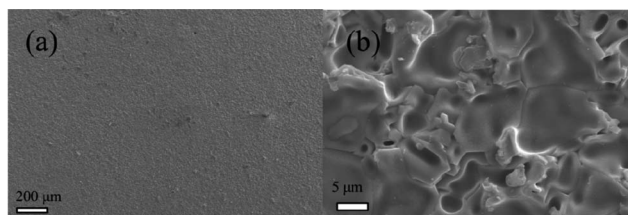


Fig. 5 SEM images of a dense SNS electrolyte; (a) surface morphology; (b) cross-section.

Thermal expansion coefficient (TEC)

A good thermal expansion match between any two adjacent components in a SOFC endures the latter to repeated thermal transients. Fig. 6 shows the variation of TEC with temperature from RT to 1000 °C. The obtained average TEC = $12.1 \times 10^{-6} \text{ K}^{-1}$ is deemed manageable with the most active electrode materials. The TEC mismatch issue can also be mitigated if high-TEC electrodes are dispersed as nanoparticles and supported by a SNS skeleton as demonstrated in this study.

With an excellent oxide-ion conductor identified, lowering electrode polarizations would be the next priority to achieve the ultimate high power density of a SOFC. As described in the Experimental section, a co-sintered symmetrical structure consisting of a thick SNS membrane coated with two thin identical porous SNS scaffolds impregnated with active electrode nanoparticles was adopted as the electrode for reducing electrode polarizations. The cross-sectional views of the three-layer microstructures are shown in Fig. 7. From these SEM images, it is evident that submicron SSC particles are well-connected and dispersed within the SNS skeleton, which ensures good oxygen reduction reaction activity and electronic conductivity.

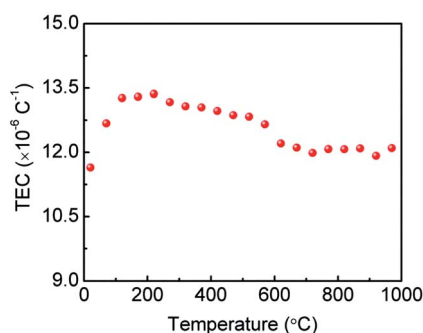


Fig. 6 Thermal expansion coefficient of SNS measured from RT to 1000 °C.

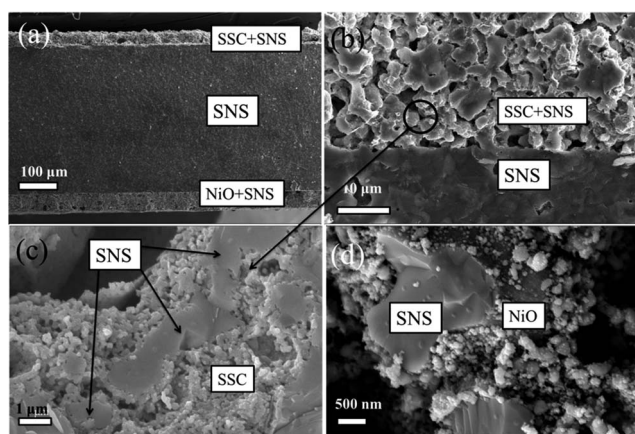


Fig. 7 Microstructures of a SNS-supported SOFC; (a) overall view of the three functional layers; (b) cathode view; (c) magnified cathode view; (d) magnified anode view.

The performance of a composite cathode SSC/SNS was first evaluated by EIS using the symmetrical cell configuration as described in the Experimental section. Fig. 8 shows the spectra measured at 600 °C in air. To show the advantage of SNS over LSGM, a similarly structured LSGM symmetrical cell with the same thickness ($\sim 230 \mu\text{m}$ for this case) and infiltrated cathode SSC was also made and tested. The comparison shown in Fig. 8 indicates an ohmic resistance of $0.350 \Omega \text{ cm}^2$ for SNS, but as high as $0.664 \Omega \text{ cm}^2$ for LSGM, at 600 °C. The difference in electrode polarization is even more revealing: $0.266 \Omega \text{ cm}^2$ for the SNS-cell and $0.784 \Omega \text{ cm}^2$ for the LSGM-cell. Higher oxide-ion conductivity of SNS clearly plays a key role in reducing ohmic and electrode polarization resistances observed.

The electrochemical performance of a $294 \mu\text{m}$ thick SNS-supported single SOFC with infiltrated electrode nanoparticles was evaluated from 500 to 600 °C, the results of which are shown in Fig. 9. The peak power density reached 431 mW cm^{-2} at 600 °C and 213 mW cm^{-2} at 500 °C, respectively. The power densities observed at such intermediate temperatures for a SOFC with such a thick electrolyte membrane are very impressive. Compared to the best peak power density reported for a $200 \mu\text{m}$ LSGM-based SOFC, *viz.* 200 mW cm^{-2} at 600 °C,²¹ this performance represents a more than 2-fold power enhancement. As the temperature and the thickness of the electrolyte are further reduced, which is an ongoing research study in the authors' lab, the degree of the enhancement would be even greater. The appreciable power enhancement is believed to be closely associated with the high ionic conductivity and low activation energy of the SNS electrolyte.

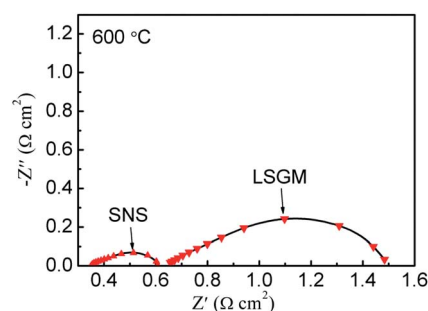


Fig. 8 Comparison of EIS spectra of SSC-SNS/SNS/SSC-SNS and SSC-LSGM/LSGM/SSC-LSGM symmetrical cells measured in air.

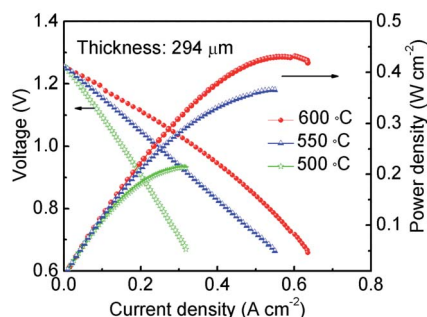


Fig. 9 Electrochemical performance of a $294 \mu\text{m}$ thick SNS-supported SOFC with infiltrated electrode nanoparticles.

Conclusions

In summary, the newly discovered 2D layered $\text{Sr}_{3-3x}\text{Na}_{3x}\text{Si}_3\text{O}_{9-1.5x}$ ($x = 0.45$) (SNS) has been fully characterized as an electrolyte material for IT-SOFCs. Its oxide-ion conductivity is the highest with the lowest activation energy among all the chemically stable oxide-ion conductors reported. The purity of oxide-ion conduction has also been confirmed by the dependence of ionic conductivity on pO_2 . The stable ionic conductivity over time further illustrates its potential to be a practical electrolyte for commercial IT-SOFCs. The electrochemical performance of a 294 μm thick-film SNS-supported SOFC is very promising, reaching peak power densities of 431 and 213 mW cm^{-2} at 600 and 500 $^\circ\text{C}$, respectively. Overall, it is concluded that SNS is a superior oxide-ion conductor well suited for IT-SOFCs. Considering its competitive costs in materials and manufacturing and rare-earth free composition, SNS has great potential to become a new class of technologically and strategically important electrolytes for commercial IT-SOFCs.

Acknowledgements

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