Perovskite Sr0.9Fe0.9Zr0.1O3- : Redox-stable Structure, Oxygen Vacancy, Electrical Properties and Steam Electrolysis Performance (Postprint)

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Date: 2017-11-05T00:00:00+00:00

Abstract

Many researchers have studied on perovskite oxide for its unique structure. Perovskite oxides, ABO3- , with different A and B metals have shown wide applications in many fields, in particular solid oxide electrolysers. SrFeO3- , typical perovskite oxides, in which iron is the mixed-valence cation with the capacity to change the chemical valence, have a wide range of oxygen nonstoichiometry. In this study, Sr0.9Fe0.9Zr0.1O3- (SFZO) is synthesized and then treated in 5%H2/Ar and air at high temperature, exhibiting excellent redox stability. Redox-stable structure, oxygen vacancy and electrical properties of SFZO are investigated. Steam electrolysis is then performed with SFZO cathode under 5%H2O/5%H2/Ar and 5%H2O/Ar atmospheres, respectively. The present results indicate that the SFZO is a novel promising cathode material for solid oxide steam electrolyser.

Full Text

Abstract

Perovskite oxides with the general formula ABO have attracted considerable attention due to their unique structural properties. These materials exhibit remarkable flexibility, allowing mixed-valence transition metal cations to undergo valence changes and accommodate varying concentrations of oxygen vacancies. This structural adaptability has enabled their application across diverse fields including oxygen permeable membranes, photocatalysis, magnetic materials, solid oxide fuel cells (SOFCs), and solid oxide electrolysis cells (SOECs). SrFeO represents a typical perovskite oxide containing mixed-valence iron cations (Fe) at the B-site that can reduce to lower valence states under low oxygen partial pressure, accompanied by oxygen vacancy formation. However, under strongly reducing conditions, strontium ferrates undergo a phase transformation from cubic perovskite to orthorhombic brownmillerite structure, where oxygen vacancies aggregate and become ordered, severely compromising oxide ion conduction and electrical conductivity.

In this work, we synthesized Zr-doped perovskite Sr . Fe . Zr . O (SFZO) via solid-state reaction to suppress this detrimental phase transition. The material demonstrates excellent redox stability when treated in 5%H /Ar and air at high temperatures. We systematically investigated the redox-stable structure, oxygen vacancy characteristics, and electrical properties of SFZO, and subsequently evaluated its performance as a cathode material for steam electrolysis under both 5%H O/5%H /Ar and 5%H O/Ar atmospheres. The results indicate that SFZO is a promising novel cathode material for solid oxide steam electrolyzers.

Keywords: phase structure; solid oxide electrolyzer; Sr . Fe . Zr . O ; cathode; steam electrolysis
DOI: 10.14102/j.cnki.0254-5861.2011-1716

1 Introduction

Perovskite oxides (ABO) have attracted extensive research interest for many years due to their distinctive crystal structure. These materials offer remarkable structural flexibility, enabling mixed-valence transition metal cations to undergo valence state changes while simultaneously accommodating variable oxygen vacancy concentrations. Consequently, ABO oxides have demonstrated fascinating properties and found applications in numerous fields, including oxygen permeable membranes, photocatalysis, magnetic materials, solid oxide fuel cells (SOFCs), and solid oxide electrolysis cells (SOECs).

SrFeO , a typical perovskite oxide, contains mixed-valence iron cations at the B-site, primarily as Fe , which can transform to lower valence states under reduced oxygen partial pressure, accompanied by oxygen vacancy formation. However, strontium ferrates are known to undergo phase transformation from cubic to orthorhombic brownmillerite structure under relatively strong reducing atmospheres, where oxygen vacancies aggregate and eventually become ordered. While oxygen vacancies in perovskites generally exist as point defects and significantly influence structural and electronic properties, excessive vacancy concentrations can be detrimental. An appropriate amount of oxygen vacancies facilitates oxygen-ion transport and yields favorable electronic properties, but sufficiently high concentrations can cause vacancy aggregation, ordering, and even phase transformation, drastically reducing oxide ion conduction and electrical conductivity.

To address this challenge, we synthesized Zr-doped perovskite Sr . Fe . Zr . O (SFZO) using the solid-state reaction method to suppress phase transition. We systematically studied the structure, oxygen vacancies, electrical properties, and electrochemical performance of SFZO, and subsequently performed steam electrolysis using SFZO cathodes.

2 Experimental

2.1 Materials and Apparatus

Perovskite Sr . Fe . Zr . O (SFZO) powder was prepared by conventional solid-state reaction. Stoichiometric amounts of SrCO , Fe O , and ZrO (all chemicals were 99% analytical grade from Sinopharm Chemical Reagent Co., Ltd) were thoroughly mixed by grinding in a zirconia ball mill for 10 minutes at 1000 rpm, pressed into pellets, and calcined in air at 1300 °C for 20 hours. The SFZO samples were subsequently reduced in 5%H /Ar at 800 °C for 3 hours.

Phase analysis of the as-synthesized SFZO powder was performed by X-ray diffraction (XRD) at room temperature using a D/MAX2500V diffractometer (Rigaku Corporation, Japan) with Cu K radiation (2 = 20–80°) at a scan rate of 3° min^{1}. The surface microstructure of the electrolyzer was examined by scanning electron microscopy (SEM, JSM-6490LV, JEOL Ltd, Japan). Transmission electron microscopy (TEM) analysis was conducted on oxidized SFZO powder using a JEOL 2100F field-emission transmission electron microscope operating at 200 kV. X-ray photoelectron spectroscopy (XPS, Al K , ESCALAB25, Thermo, USA) was employed to analyze the chemical states of elements on the SFZO surface before and after high-temperature treatment in 5%H /Ar at 800 °C for 3 hours. Thermogravimetric analysis (TGA) of reduced SFZO powder was performed using a thermal analyzer (STA449F3, Naichi Corporation, Germany) in air from 320 to 1000 °C at a heating rate of 5 °C min^{1}. Electrical conductivities were measured using a direct current four-probe method with an electrochemical workstation (Keithley 2000 Digital Multimeter, Keithley Instruments Inc., USA) in both air and reducing (5%H /Ar) atmospheres at temperatures ranging from 650 to 800 °C. The dependence of conductivity on oxygen partial pressure was measured at 800 °C using an online multimeter (Keithley 2000) while oxygen partial pressure was monitored from 10^{1} to 100 atm using an online oxygen sensor (OXYGEN-MODEL 3000-SX).

2.2 Symmetrical Cell Preparation

A 2-mm-thick 8YSZ electrolyte support was prepared by dry-pressing 8YSZ powders into 20-mm-diameter disks followed by sintering in air at 1550 °C for 20 hours. Both surfaces of the YSZ electrolyte support were mechanically polished and ultrasonically cleaned in ethanol and acetone. Ce . Sm . O (SDC) powders were prepared by combustion synthesis, in which Sm O and Ce(NO) ·6H O powders were mixed uniformly and sintered at 800 °C (3 °C min^{1}) for 3 hours in air. Cathode slurry was prepared by mixing SFZO-SDC powder (65:35 wt%), alpha-terpineol, and appropriate amounts of cellulose additive. The slurry was then screen-printed onto both surfaces of the cleaned YSZ discs (area 0.5 cm^2) and sintered in air at 1100 °C for 3 hours to assemble symmetrical cells. Silver paste (SS-8060, Xinluyi, Shanghai, China) was applied as a current collector covering both electrode surfaces, and silver wire (0.2 mm diameter) was used for electrical connections, followed by firing in air at 550 °C for 30 minutes. The symmetrical cells (SFZO-SDC/YSZ/SFZO-SDC) were characterized by electrochemical impedance spectroscopy using a workstation (IM6, Zahner, Germany) at open circuit voltage (OCV) at 800 °C under various hydrogen and oxygen partial pressures. The frequency range was 100 mHz–4 MHz with a voltage amplitude of 10 mV, and gas flow rates were controlled at 50 ml min ^{1} using a mass flow meter (D08-5F, Sevenstar, Beijing, China).

2.3 Electrolysis Cell Preparation

(La . Sr .) . MnO (LSM) powders were synthesized by solid-state reaction from appropriate amounts of La O , SrCO , and MnO at 1100 °C (3 °C min ^{1}) for 10 hours in air. LSM slurry was prepared by mixing LSM-SDC powder (65:35 wt%), alpha-terpineol, and cellulose additive. SFZO-SDC slurry was printed onto the cathode surface and LSM slurry onto the anode surface of YSZ discs (area 0.2 cm^{2}), followed by sintering in air at 1100 °C for 3 hours to assemble single solid oxide cells (SFZO-SDC/YSZ/LSM-SDC). The single solid-oxide electrolyzers were sealed to a home-made testing apparatus using ceramic paste (JD-767A, Jiudian, Dongguan, China) for electrochemical measurements including AC impedance and current-voltage (I-V) characterization. The electrolyzers were investigated for direct hydrogen production via steam electrolysis, with H yield analyzed by gas chromatography (GC-2014, SHIMADZU, Japan) at each applied voltage.

3 Results and Discussion

3.1 Crystal Structure Analysis

Fig. 1 [Figure 1: see original paper] shows XRD patterns of oxide powders calcined at 1300 °C in air for 20 hours, confirming that both perovskite-type SrFeO and SFZO form pure phases. However, as shown in Fig. 1(a), SrFeO undergoes a phase transition from cubic perovskite to orthorhombic brownmillerite structure (Sr Fe O) after reduction, indicating poor phase stability in reducing atmospheres. In contrast, Fig. 1(b) demonstrates that SFZO exhibits no phase transitions or impurities even after treatment at 800 °C in 5%H /Ar for 3 hours. The partial substitution of Fe with Zr effectively enhances the phase stability of SFZO even under strongly reducing conditions. Using the Scherrer equation L = K / cos , the lattice parameter of oxidized SFZO is determined to be 3.908 Å, slightly smaller than that of reduced SFZO (3.921 Å). This expansion upon reduction arises from the partial reduction of Fe (0.585 Å) to Fe^{3} (0.645 Å) and the associated oxygen loss at high temperature.

3.2 Oxygen Vacancy and Transition Metal Analysis

Fig. 2 Figure 2: see original paper presents TGA results for reduced SFZO heated from 320 to 1000 °C (5 °C min ^{1}) in air. In the 320–476 °C range, weight gain corresponds to oxidation of Fe^{3} to higher valence states (Fe) with concurrent oxygen incorporation, amounting to 0.156 mol oxygen per formula unit. In the 476-1000 °C range, weight loss occurs due to reduction of Fe to Fe^{3} and lattice oxygen loss, with 0.121 mol oxygen lost per formula unit at high temperature. This thermally induced oxygen loss creates oxygen vacancies above 476 °C, and charge compensation drives the Fe valence change from 4+ to 3+. Fig. 2(b) shows typical microstructures with a lattice constant of 0.383 nm, consistent with reported values for the (111) plane.

XPS analysis was performed to confirm valence state changes in oxidized and reduced SFZO samples. All spectra were fitted using Shirley-type background subtraction with 80% Gaussian and 20% Lorentzian functions, and peak information was referenced from the Thermo Fisher Scientific database. As shown in Fig. 3 Figure 3: see original paper, the Fe 2p spectrum of oxidized SFZO deconvolutes into three spin-orbit doublets: Fe^{2} at 709.9 eV (2p /) and 722.78 eV (2p /), an intermediate Fe^{2} /^{3} state at 710.4 eV (2p /) and 723.5 eV (2p /), and Fe at 711.4 eV (2p /) and 725.08 eV (2p /). In reduced SFZO (Fig. 3(b)), peaks for Fe^{2} (2p /), Fe^{3} (2p /), Fe^{2} (2p /), and Fe^{3} (2p /) appear at 714.70, 711.88, 728.08, and 724.88 eV, respectively, with a Fe^{2} /Fe^{3} ratio of approximately 2.1. The binding energy shift between oxidized and reduced samples reflects the Fe^{3} →Fe valence change and associated lattice oxygen variation, consistent with TGA results.

3.3 Electrical and Electrochemical Properties

Fig. 4 Figure 4: see original paper shows the temperature-dependent conductivity of SFZO, which exhibits metallic behavior with values reaching approximately 7.0 S cm ^{1} in air and 1.5 S cm ^{1} in 5%H /Ar at 800 °C. Notably, the conductivity of reduced SFZO exceeds reported values for LSCM at high temperatures. Fig. 4(b) illustrates the conductivity dependence on oxygen partial pressure at 800 °C, increasing from 0.3 to 7.0 S cm ^{1} as pO increases from 10 ^{1} to 100 atm. SFZO exhibits typical p-type conduction, though minor n-type behavior appears at low oxygen partial pressure due to reversible Fe /^{3} /^{2} transitions. The conductivity decrease in reducing atmospheres results from reduced charge carrier concentration and increased oxygen vacancy concentration.

Fig. 5 Figure 5: see original paper and (b) present AC impedance spectra for symmetrical SFZO-SDC/YSZ/SFZO-SDC cells tested under various hydrogen and oxygen partial pressures, respectively. Ohmic resistance (R) was subtracted to compare electrode polarization resistances (R), determined from the real-axis intercept using ZView software. As shown in Fig. 5(a), R decreases from 5.74 to 2.29 Ω cm^{2} as hydrogen partial pressure increases from 5% to 100%, indicating that reducing atmospheres enhance electrode performance. Under varying oxygen partial pressures (Fig. 5(b)), R values are 0.71, 0.51, 0.39, and 0.30 Ω cm^{2} at 2%, 5%, 10%, and 20% O , respectively, demonstrating SFZO' s potential as both cathode and anode in SOECs.

Fig. 6 Figure 6: see original paper shows the microstructure of a single electrolyzer with the configuration (cathode) SFZO-SDC/YSZ/LSM-SDC (anode).

The porous electrode layers are approximately 10 m thick and exhibit good adhesion to the YSZ electrolyte. Steam electrolysis was performed at 800 °C with cathode feeds of 5%H O/5%H /Ar and 5%H O/Ar at applied voltages of 1.0–2.0 V. Fig. 6(b) presents typical current density-voltage (I-V) curves. Open circuit voltages (OCV) of ~100 mV (5%H O/Ar) and ~1.1 V (5%H O/5%H /Ar) confirm proper gas sealing. Two distinct processes occur: (a) electrochemical reduction/oxidation of electrodes at low voltages, and (b) steam electrolysis at high voltages. Above 1.1 V, current densities increase steeply in both atmospheres, indicating that Zr doping significantly enhances phase stability and cell performance under reducing conditions. The current density increases from ~7.8 to 325 mA cm ^{2} at 1.0–2.0 V with 5%H O/Ar feed, reaching a maximum of 326 mA cm ^{2} at 2.0 V with 5%H O/5%H /Ar.

In situ AC impedance spectroscopy was employed to investigate polarization resistance under various applied voltages. Fig. 7 [Figure 7: see original paper] shows impedance spectra for SFZO-based electrolyzers at 800 °C from 1.2 to 1.7 V in both atmospheres. Two main electrochemical processes occur in this voltage range: cathode reduction at low voltages and steam electrolysis at high voltages. In 5%H O/5%H /Ar (Fig. 7(a1, a2)), R decreases significantly with increasing voltage from 1.2 to 1.7 V, as higher potentials electrochemically reduce the cathode, increasing mixed conductivity and enhancing performance. The impedance spectra show two semicircles: high-frequency arcs (R) and low-frequency arcs (R). R remains stable, indicating consistent high-frequency charge transfer, while R decreases slightly from 3.74 to 3.67 Ω cm^{2}, suggesting improved gas conversion kinetics. Similar behavior in 5%H O/Ar (Fig. 7(b1, b2)) indicates adequate oxygen vacancy concentrations even in less reducing atmospheres.

Fig. 8 Figure 8: see original paper and (b) compare electrolysis performance of SFZO cathodes in both atmospheres at 800 °C. Current densities reach approximately 78, 207, and 265 mA cm ^{2} at 1.2, 1.6, and 1.8 V in 5%H O/5%H /Ar, and 98, 212, and 266 mA cm ^{2} at corresponding voltages in 5%H O/Ar. The SFZO cathode demonstrates similar performance in both atmospheres with stable operation across a wide voltage range, confirming excellent phase stability under strongly reducing conditions at high temperature. This performance is comparable to reported values of 41–173 mA cm ^{2} at 1.2–2.0 V for 2-mm-thick YSZ electrolyte-supported cells with Co O -loaded LSM-BCZYZ cathodes.

Fig. 8(c) and (d) present hydrogen production rates and current efficiencies for SFZO composite cathodes. Hydrogen production rates reach 0.7–1.4 mL cm ^{2} min ^{1} at 1.2–2.0 V in 5%H O/5%H /Ar, and 0.7–1.9 mL cm ^{2} min ^{1} in 5%H O/Ar (approximately 30% higher). Current efficiency reaches 80% in 5%H O/Ar versus 70% in 5%H O/5%H /Ar at 1.6–2.0 V, though it achieves 90% at low voltages in 5%H O/5%H /Ar due to enhanced catalytic activity in more reducing conditions. As SFZO is a p-type conductor with conductivity approximately one order of magnitude higher in oxidizing versus reducing atmospheres, the lower conductivity in 5%H O/5%H /Ar may explain the reduced current efficiency at high voltages compared to 5%H O/Ar.

4 Conclusion

This work demonstrates perovskite SFZO as a redox-stable cathode material for solid oxide steam electrolyzers. Excellent phase stability is achieved with only 10% Zr doping in the Fe-based perovskite, maintaining an appropriate oxygen vacancy concentration. Electrical characterization reveals typical p-type conductivity of 1.5 S cm^{1} in 5%H /Ar and 7.0 S cm^{1} in air at 800 °C. The SFZO oxide exhibits superior SOEC cathode performance, achieving current efficiencies up to 90% for steam electrolysis in 5%H O/5%H /Ar at low voltages. These results highlight the enormous potential of SFZO for direct steam electrolysis applications.

REFERENCES

(1) Patrakeev, M. V.; Mitberg, E. B.; Lakhtin, A. A.; Leonidov, I. A.; Kozhevnikov, V. L.; Kharton, V. V.; Avdeev, M.; Marques, F. M. B. Oxygen nonstoichiometry, conductivity, and seebeck coefficient of La . Sr . Fe Ga O . perovskites. *J. Solid State Chem.* **2002**, *157*, 203-213.

(2) Alonso, J. A.; Martínez-Lope, M. J.; Casais, M. T.; MacManus-Driscoll, J. L.; Silva, P. S. I. P. N.; Cohen, L. F.; Fernández-Díaz, M. T. Non-stoichiometry, structural defects and properties of LaMnO with high values (0.11 0.29). *J. Mater. Chem.* **1997**, *7*, 2139-2144.

(3) Eichel, R. Structural and dynamic properties of oxygen vacancies in perovskite oxide-analysis of defect chemistry by modern multi-frequency and pulsed EPR techniques. *Phys. Chem. Chem. Phys.* **2011**, *13*, 368-384.

(4) Jaiswal, S. K.; Kumar, J. Oxygen permeation characteristics of sol-gel derived barium-substituted strontium ferrite membranes. *J. Am. Ceram. Soc.* **2017**, *100*, 1306-1312.

(5) Kanhere, P.; Chen, Z. A review on visible light active perovskite-based photocatalysts. *Molecules* **2014**, *19*, 19995-20022.

(6) Ahmed, T.; Chen, A.; Yarotski, D. A.; Trugman, S. A.; Jia, Q.; Zhu, J. X. Magnetic, electronic, and optical properties of double perovskite Bi FeMnO . *Apl. Mater.* **2017**, *5*, 35601-35608.

(7) Gan, L. Z.; Xie, K. Electricity storage with high roundtrip efficiency in a reversible solid oxide cell stack. *Chin. J. Chem. Phys.* **2016**, *29*, 517-522.

(8) Ye, L. T.; Zhang, M. Y.; Huang, P.; Guo, G. C.; Hong, M. C.; Li, C. S.; Irvine, J. T. S.; Xie, K. Enhancing CO electrolysis through synergistic

control of non-stoichiometry and doping to tune cathode surface structures. *Nat. Commun.* **2017**, *8*, 14785-14794.

(9) Patrakeev, M. V.; Leonidov, I. A.; Kozhevnikov, V. L.; Kharton, V. V. Ion-electron transport in strontium ferrites: relationships with structural features and stability. *Solid State Sci.* **2004**, *6*, 907-913.

(10) Li, Z.; Li, S. S.; Tseng, C. J.; Tao, S. W.; Xie, K. Redox-reversible perovskite ferrite cathode for high temperature solid oxide steam electrolyser. *Electrochim. Acta* **2017**, *229*, 48-54.

(11) Kostogloudis, G. C.; Ftikos, C. Properties of A-site-deficient La . Sr . Co . Fe . O - based perovskite oxides. *Solid State Ionics* **1999**, *126*, 142-151.

(12) Santos-Gómez, L.; Compana, J. M.; Bruque, S.; Losilla, E. R.; Marrero-López, D. Symmetric electrodes for solid oxide fuel cells based on Zr-doped SrFeO . *J. Power Sources* **2015**, *279*, 419-427.

(13) Monshi, A.; Foroughi, M. R.; Monshi, M. R. Modified Scherrer equation to estimate more accurately nano-crystallite size using XRD. *World J. Nano. Sci. Eng.* **2012**, *2*, 154-160.

(14) David, N. M.; Roger, A. D. S.; Han-Ill, Y.; Manfred, M. Phase stability and oxygen nonstoichiometry of highly oxygen-deficient perovskite-type oxides: a case study of (Ba, Sr)(Co, Fe)O . *Chem. Mater.* **2012**, *24*, 269-274.

(15) Patra, H.; Rout, S. K.; Pratihar, S. K.; Bhattacharya, S. Thermal, electrical and electrochemical characteristics of Ba Sr Co . Fe . O cathode material for intermediate temperature solid oxide fuel cells. *Int. J. Hydrogen Energy* **2011**, *36*, 11904-11923.

(16) Li, Z.; Wei, B.; Lu, Z.; Huang, X.; Su, W. Structure, electrical and thermal properties of (Ba . Sr .) Gd Co . Fe . O perovskite as a solid-oxide fuel cell cathode. *Solid State Ionics* **2012**, *207*, 38-43.

(17) Zhang, Z.; Chen, D.; Shao, Z. Efficient and CO -tolerant oxygen transport membranes prepared from high-valence B-site substituted cobalt-free SrFeO . *J. Memb. Sci.* **2015**, *495*, 187-197.

(18) Ghaffari, M.; Huang, H.; Tan, O. K.; Shannon, M. Band gap measurement by ultraviolet photoelectron spectroscopy and photovoltage method. *Cryst. Eng. Comm.* **2012**, *14*, 7487-7492.

(19) Xiao, G.; Liu, Q.; Wang, S.; Komvokis, V. G.; Amiridis, M. D.; Heyden, A.; Ma, S.; Chen, F. Synthesis and characterization of Mo-doped SrFeO as cathode materials for solid oxide fuel cells. *J. Power Sources* **2012**, *202*, 63-69.

(20) Qin, Q.; Wu, G.; Chen, S.; Doherty, W.; Xie, K.; Wu, Y. Perovskite titanate cathode decorated by in-situ grown iron nanocatalyst with en-

hanced electrocatalytic activity for high-temperature steam electrolysis. *Electrochim. Acta* **2014**, *127*, 215–227.

(21) Zhang, J.; Xie, K.; Zhang, Y.; Yang, L.; Wu, G.; Qin, Q.; Li, Y.; Wu, Y. Composite titanate cathode decorated with heterogeneous electrocatalytic sites towards efficient carbon dioxide electrolysis. *RSC Adv.* **2014**, *4*, 22697–22709.

(22) Yuan, H.; Zhang, L.; Xu, M.; Du, X. Effect of sol pH on microstructures, optical and magnetic properties of (Co, Fe)-codoped ZnO films synthesized by sol-gel method. *J. Alloy Compd.* **2015**, *651*, 571–577.

(23) Lashtabeg, A.; Irvine, J. T. S.; Feighery, A. Thermomechanical and conductivity studies of doped niobium titanates as possible current collector material in the SOFC anode. *Ionics* **2003**, *9*, 220–226.

(24) Ruan, C.; Xie, K. A redox-stable chromate cathode decorated with in situ grown nickel nanocatalyst for efficient carbon dioxide electrolysis. *Catal. Sci. Technol.* **2015**, *5*, 1929–1940.

(25) Xu, S.; Dong, D.; Wang, Y.; Doherty, W.; Xie, K. Perovskite chromates cathode with resolved and anchored nickel nano-particles for direct high-temperature steam electrolysis. *J. Power Sources* **2014**, *246*, 346–355.

(26) Li, S.; Yan, R.; Wu, G.; Xie, K.; Cheng, J. Composite oxygen electrode LSM-BCZYZ impregnated with Co O nanoparticles for steam electrolysis in a proton-conducting solid oxide electrolyzer. *Int. J. Hydrogen Energy* **2013**, *38*, 14943–14951.

Figure Captions

Fig. 1. XRD patterns of samples: (a) oxidized and reduced SrFeO ; (b) oxidized and reduced SFZO. Schematics of (c) cubic perovskite and (d) orthorhombic brownmillerite structures (A = Sr, green; B = Fe/Zr, yellow; O = oxygen, red).

Fig. 2. (a) TGA of reduced SFZO from 320 to 1000 °C in air; (b) TEM image of reduced SFZO powder.

Fig. 3. XPS Fe spectra for (a) oxidized and (b) reduced SFZO samples.

Fig. 4. Conductivity dependence of SFZO on (a) temperature in air and 5%H /Ar (650–800 °C); (b) oxygen partial pressure (100–10^{1} atm) at 800 °C.

Fig. 5. AC impedance of symmetrical SFZO-SDC/YSZ/SFZO-SDC cells at 800 °C under (a) different hydrogen partial pressures and (b) different oxygen partial pressures.

Fig. 6. (a) SEM image of electrolyzer cell: SFZO-SDC/YSZ/LSM-SDC; (b) I-V curves for solid oxide electrolyzer with SFZO composite cathode for steam electrolysis at 800 °C in 5%H O/5%H /Ar and 5%H O/Ar.

Fig. 7. In situ AC impedance of SFZO-based symmetrical electrolyzers at 800 °C with (a1, a2) 5%H O/5%H /Ar and (b1, b2) 5%H O/Ar feeds.

Fig. 8. Performance of single electrolyzer with SFZO cathode at different potentials for steam electrolysis in (a) 5%H O/5%H /Ar and (b) 5%H O/Ar. Hydrogen production rate (c) and current efficiency (d) for electrolyzers with 5%H O/5%H /Ar and 5%H O/Ar feeds at 800 °C.