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RESEARCH ARTICLE

INVESTIGATION OF EFFECTS OF CO DOPING ON THE ELECTROCHEMICAL BEHAVIOUR OF DOUBLE PERVOSKITE OXIDE $Sr_2MgCrO_{6-\delta}$ AS AN ANODE MATERIAL FOR SOLID OXIDE FUEL CELLS

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ABSTRACT

Double-perovskite materials of composition $Sr_2Mg_{1-x}Co_xCrO_{6-\delta}$ (SMCCO, x = 0 to 0.7) were evaluated as potential SOFC anode materials. Their lattice structures, electrical and ionic conductivity, and electrochemical performance were investigated to study the effect of Co content. SMCCO also showed good chemical compatibility at temperatures below 1000 °C. Both the electronic and ionic conductivity increased with increasing Co doping. To investigate the effect of Co doping on the conduction properties of SMCCO, we performed first-principle calculations. From these results, we found that the weak Co O bond is considered to be responsible for the enhanced ionic conductivity of SMCCO materials. The substitution of Co was also found to increase the sinterability of SMCCO, resulting in a decrease in the polarization resistance of the SMCCO electrode. Single-cell tests indicated the potential ability of the Co-doped SMCO to be used as SOFC anodes.

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INTRODUCTION

The fuel cell is a well-known device that directly and efficiently converts chemical energy to electrical energy. Of the various fuel cell types, the solid-oxide fuel cell (SOFC) is considered to have the greatest potential for large-scale power generation; however, one of the difficulties faced in the improvement of the current state-of-the-art SOFCs is related to the need for a suitable anode that can operate not only with pure H_2 gas but also with low-cost and more abundant fuels such as natural gas. (Sun and Stimming, 2007; Steele and Heinzel, 2001; Singh and Minh, 2004; Brandon *et al*., 2003; Singhal, 2002; Haile, 2003; Minh, 2004) Although the conventional anode material, Ni-YSZ, exhibits excellent catalytic activity and current collection, it suffers from carbon deposition and sulphur poisoning when using hydrocarbon as fuels. It also shows low tolerance to redox cycles, which make this anode vulnerable to exposure to high oxygen partial pressure environments. (Atkinson *et al*., 2004; Mclntosh and Gorte, 2004; Jiang *et al*., 2004; Fergus, 2006; Tao and Irvine, 2004; Goodenough and Huang, 2007) In recent years, mixed ionic and electronic conductors have been investigated as potential anode materials considering their high resistance to sulphur poisoning and carbon deposition, high thermo chemical stability, and extended triple-phase boundary (TPB). They are principally chromite-based and titanate-based perovskites. Doped $SrTiO_3$ was reported to have high electronic and ionic conductivity and showed good resistance to carbon deposition. However, the low catalytic activity and the poor redox stability limited the cell performance. (Miller and Irvine, 2011; Fagg *et al*., 2001; Hui and Petric, 2002; Vincent *et al*., 2010) Although chromite-based anode ($La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$) exhibited good performance when operating in pure H_2 and CH_4 at high temperatures, fuels containing H_2S would deteriorate its operating performance. (Tao and Irvine, 2003; Pena-Martínez *et al*., 2006; Lu and Zhu, 2007) Recently, the B-site-ordered double-perovskite $Sr_2MgMoO_{6-\delta}$ (SMMO) reported by Huang *et al.* has attracted great interest as a candidate anode material for solid oxide fuel cells. (SOFCs). (Huang *et al*., 2006; Huang *et al*., 2006) This material was reported with suitable chemical stability and good resistance against carbon deposition and sulphur poisoning. (Vasala *et al*., 2010; Marrero-Lopez *et al*., 2008; Ji *et al*., 2007) Unfortunately, it showed low electrical conductivity and poor electrocatalytic activity when using Ag or other non-platinum current collector, both of which lead to large anode polarization. A Substituting A and/or B site with alkali earth and transition-metal elements, respectively, offers the possibility of improving the electronic or ionic

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conductivity of Sr2MgMoO6 $_{\delta}$ as well as the catalytic properties. Doping La on the Sr-site has been reported to improve the electrocatalytic properties for fuel oxidation (Zhang and He, 2011) but deteriorates the structural stability in high oxygen partial pressure. (Vasala *et al*., 2010) Sm-doped SMMO ($Sr_{1.6}Sm_{0.4}MgMoO_{6\ \delta}$) displayed excellent electrochemical performance while maintaining structural stability. (Bi and Zhu, 2011) Doping Mn on the Mg-site could increase the electrical conductivity, but unfortunately, Mn-doped SMMO was found to be sensitive to Po_2, with the electrical conductivity rapidly decreasing with increasing oxygen partial pressure. (Huang *et al*., 2006) The electrical conductivity of Fe-substituted SMMO ($Sr_2Mg_{0.75}Fe_{0.25}MoO_{6\ \delta}$) increased, but again the material was unstable under oxidizing conditions due to phase segregation above 600 °C.[23,27] Vasala *et al*. reported that doping W and Nb on the Mo site of SMMO depressed the electrical conductivity, but a small amount of Nb could increase the ionic conductivity. (Huang *et al*., 2009) Most recently, it is reported that SMMO exhibited electrocatalytic activity toward fuels only when using Pt paste as a current collector. (Zhang *et al*., 2011)

It is well known that the 3d-block transition metals, such as Co, Ni, and Fe, normally exhibit good catalytic activity for the oxidation of H_2 and CH_4. More recently, $Sr_2CoMoO_{6\ \delta}$(SCMO), $Sr_2NiMoO_{6\ \delta}$, $A_2FeMoO_{6\ \delta}$ (A = Ca, Sr, Ba), and $Sr_2Fe_{1.5}Mo_{0.5}O_{6\ \delta}$ as anode materials containing a 3d-block transition metal were reported. The results showed that Sr_2CoMoO_6 anodes exhibited high cell power density with H_2 and CH_4 as fuels; however, it was unstable under reducing atmosphere (Liu *et al*., 2010; Wang *et al*., 2011; Zhu *et al*., 2006; Tai, *et al*., 1995; Deng *et al*., 2002). The poor stability under reducing environments is due to the weak bond between cobalt and oxygen. The structural stability of perovskite oxides is mainly determined by the stability of octahedral BO_6. A stronger B O bond usually leads to a more stable perovskite structure. (Rodríguez-Carvajal, 1993; Xie *et al*., 2011; Li *et al*., 2008) In this work, we consider the advantages of SMCCO in electrocatalytic and structural stability and develop a new anode material of Co-doped SMMO ($Sr_2Mg_{1\ x}Co_xCrO_{6\ \delta}$, SMCCO). Co was introduced into the Mg site of $Sr_2MgCrO_{6\ \delta}$ to improve the conductivity and the electrocatalytic acitivity with the premise of not deteriorating the structural stability. The effects of Co doping on the lattice structure, microstructure, thermal expansion, and electronic and ionic conductivities were systematically investigated.

Experimental

Single- phase $Sr_2Mg_{1\ x}Co_xCrO_{6\ \delta}$ (SMCCO, x = 0 to 0.7) powders were prepared via sol-gel citrate method with citric acid monohydrate as the chelating agent and $Sr(NO_3)_2$, $Mg(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$, and $Cr(NO_3)_3$ as the starting materials (all A.R. grade). The stoichiometric ratio of the total amount of citric acid monohydrate was fixed at 1:2. The resultant solution is then magnetically stirred at 80°C for 3 hours to obtain homogeneous solution which was further heated in pressure vessel at about 130°C for 12 hours until self combustion of the gel occurred and subsequently kept at 350°C for next 3 hours to eliminate the organic matter. The dehydrated powder was then ground slightly to destrol agglomerates and then calcined from 450°C to 1200°C in order to improve the crystanallity and sensitivity of the powder. Fig. 1 shows the flowchart for the preparation of nanocrystalline samples. These were then crushed to desired mesh size and then pressed in to bars and then pellets by uniaxial pressing were prepared for conductivity measurements. The phase composition and crystal structure of the samples were determined by X-ray diffraction using Cu Kα radiation. The SEM was used to observe the microstructure of the samples. The electrical conductivity of all samples was measured in air with standard four probe method in temperature range of 100-900°C,

RESULTS AND DISCUSSION

1. Phase structure Development

a. Phase Structure: Fig 2 shows the XRD patterns of $Sr_2Mg_{1\ x}Co_xCrO_{6\ \delta}$ (x=0 to 0.9). All samples can be indexed as a double-pervoskite phase with no detectable impurity peaks. Because the mixed conducting oxide used as an anode material should be stable under SOFC operating environment. As shown in Figure 2, when the doping amount of Co was at x ≤ 0.7, the samples were found to be phase pure, whereas impurities of Co_3O_4, SrO, MgO and $SrMoO_4$ were observed in the sample x=0.9. the structural stability of pervoskites oxides is primarily observed rested with the stability of octahedral BO_6. The B-O bond energy is one of the main factors that influence the stability of pervoskites oxides. The generation of impurities in the sample with x=0.9 under reducing environment is mainly due to the weak bond energy between cobalt and oxygen. More Co doping is obviously not suitable for the structural stability of SMCCO.

b. Microstructure: For microstructure study the samples with x=o to x=0.7 has been selected. Dense samples with similar relative density are required to understand the electrical conduction behaviour of SMCCO samples and to elucidate the effect of Co doping on the conductivity. Bulk density measurements indicates that the relative densities of the samples with x=0,0.1,0.3,0.5 and 0.7 are 91.26, 94.42, 95.56, 95.62 and 95.85% respectively. SEM observation (Figure 3) shows that the porosity decreases and the grain size increases with increasing Co-doping amount, indicating that Co doping improves the sinter ability of samples.

c. Characteristics of Conductivities: Figure 4 shows the total electrical conductivity as a function of temperature for $Sr_2Mg_{1\ x}Co_xCrO_{6\ \delta}$ (x=0 to 0.7) samples in air between selected temperature range. The electrical conductivity increased with increasing Co content, mainly ascribable to the electron delocalization correlated to stronger covalent characteristics of the Co-O bonds compared with Mg-O bond. The electrical conductivity of each composition except for x=0 increased with increasing temperature through a peak, then decreased. The temperature of the electrical conductivity maximum point shifted from approximately 750 to 300°C as the Co content increased form x=0.3 to 0.7, which was similar to other Co based pervoskite oxides. Figure 5 displays the Arrhenius plots of the temperature dependence of electrical conductivity. According to results the activation energy (Ea) of the samples for electron hopping decreased with increasing Co content, indicating that Co doping facilitates the conduction process of electrons.

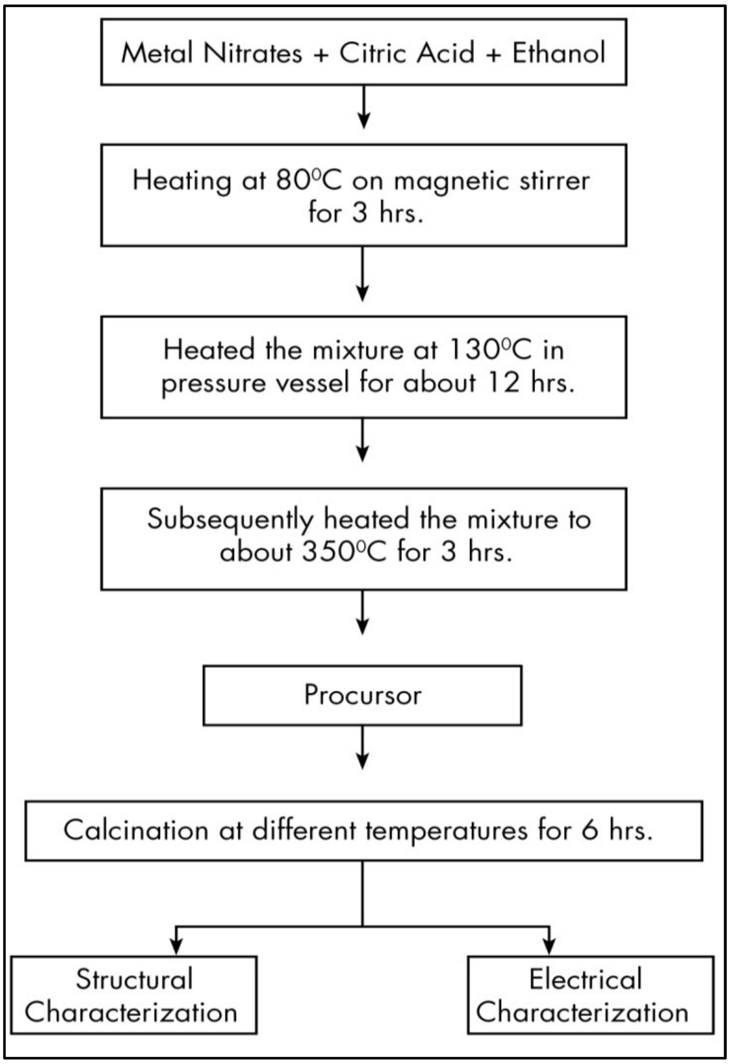


Fig. 1. Flow chart for preparation of Nanomaterials

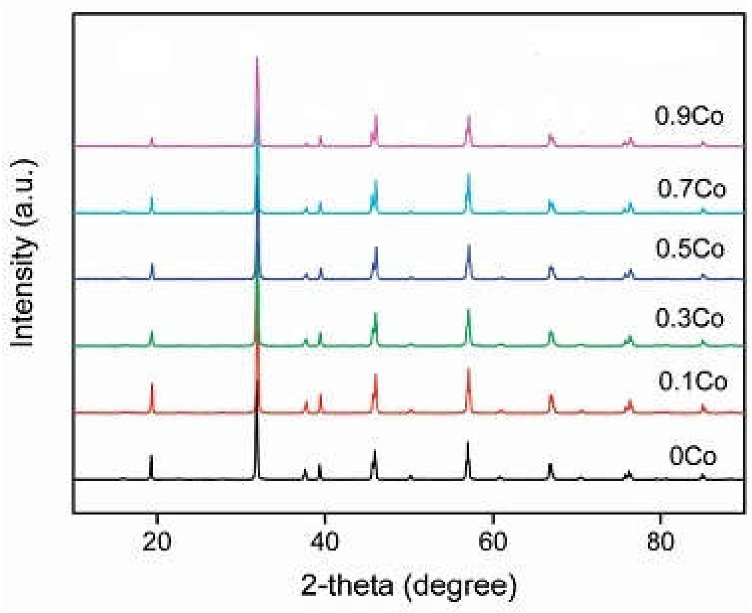


Fig.2. XRD patterns of $Sr_2Mg_{1-x}Co_xCrO_{6-\delta}$ sintered in air

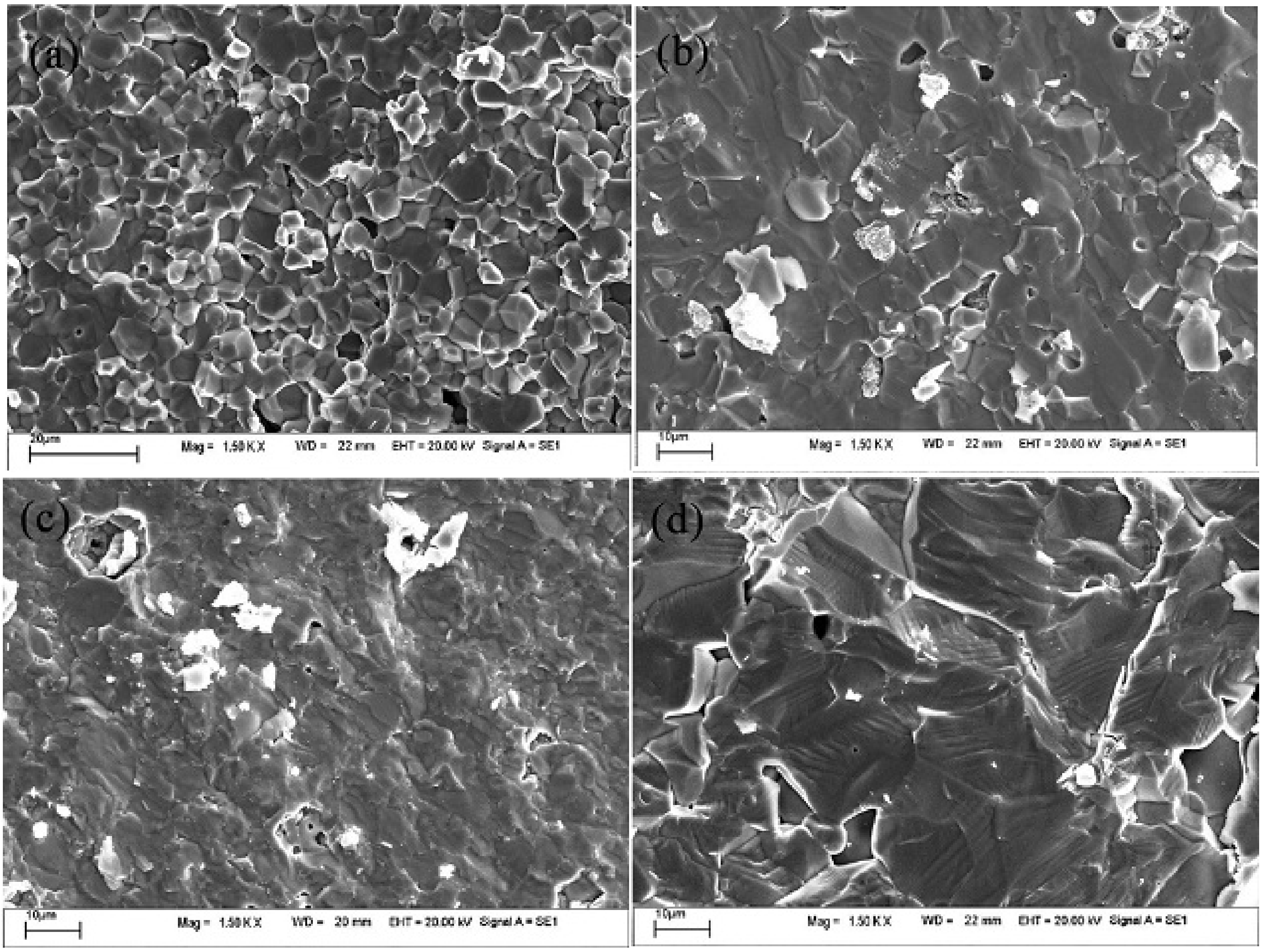


Fig.3. SEM micrographs of $Sr_2Mg_{1\ x}Co_xCrO_{6\ \delta}$ calcined at air at 800°C (a) x=0; (b) x=0.1 (c) x=0.5 (d) x=0.7

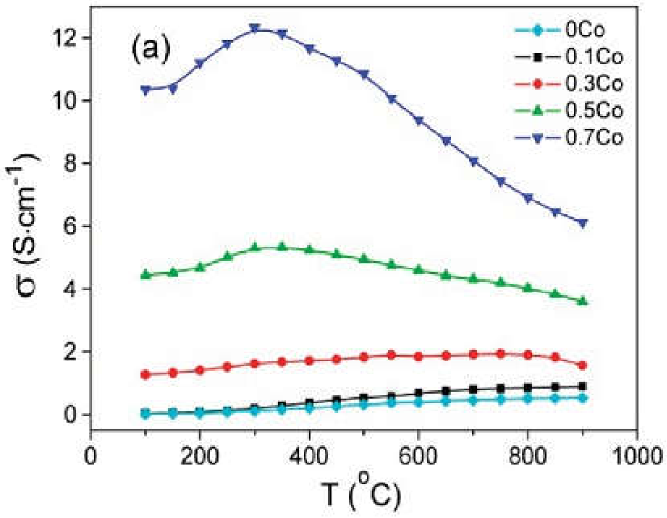


Fig. 4.

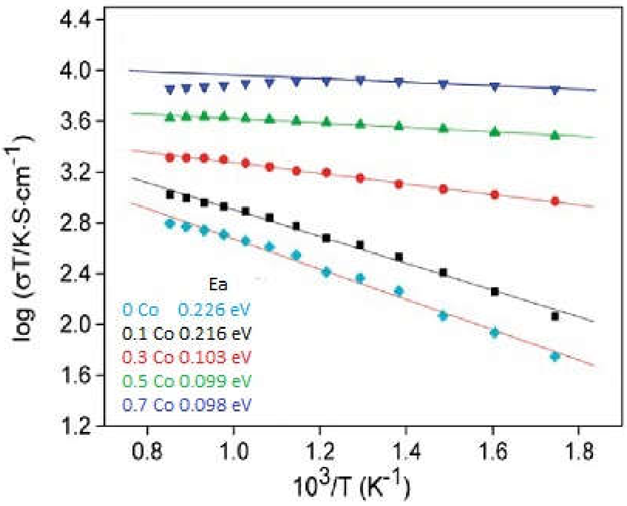
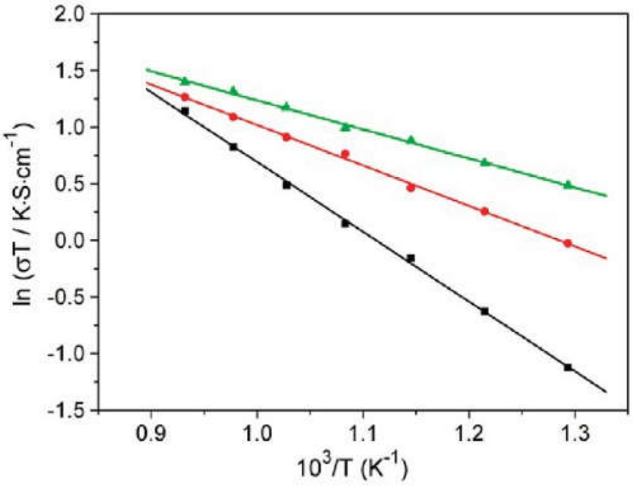


Fig. 5.

Fig.4. Electrical Conductivity of $Sr_2Mg_{1\ x}Co_xCrO_{6\ \delta}$ as function of Co doping level and temperature

Fig.5. Arrhenius plots of the electrical conductivity



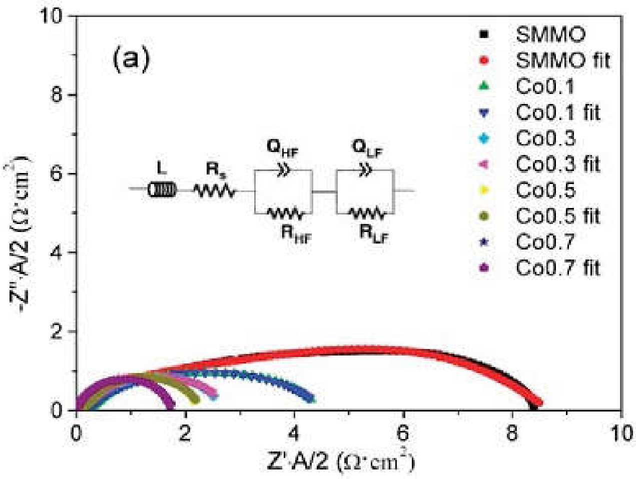


Fig.6.

Fig.7.

Fig.6. Teperature dependence of ionic conductivity of $Sr_2Mg_{1\ x}Co_xCrO_{6\ \delta}$ (x=0. 0.3,0.5, 0.7)

Fig.7. Impendance spectra of $Sr_2Mg_{1\ x}Co_xCrO_{6\ \delta}$

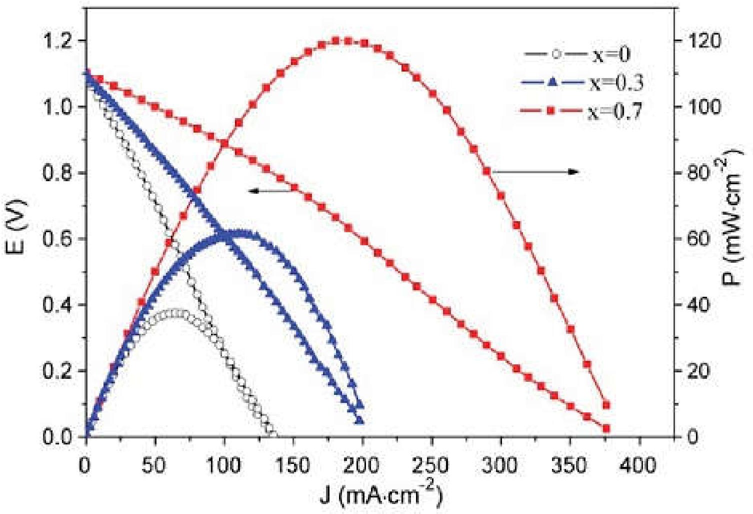


Fig.8. Cell Voltage and power density as a function of current density with different Co content

d. Ionic Conductivity: The ionic conductivity of $Sr_2Mg_{1\ x}Co_xCrO_{6\ \delta}$ (x=0. 0.3, 0.7) as a function of temperature is shown in Figure 6. The ionic conductivity increased with Co doping level. For pervoskite oxides, the ionic conductivity is primarily dependent on the concentration of Oxygen vacancies and the mobility of oxygen ions. The Co doping may increase the oxygen vacancy concentration at high temperature due to weak Co-O bond. The activation energy (Ea) for oxygen ion migration in the $Sr_2Mg_{1\ x}Co_xCrO_{6\ \delta}$ decreased remarkably with increasing Co amount.

e. Co Content Effect: The impedance measurements were carried out on series of samples $Sr_2Mg_{1\ x}Co_xCrO_{6\ \delta}$ (x=0. 0.3,0.5, 0.7) at different temperature to investigate the effect of Co on the SMCCO material. Typical Nyquist plot and equivalent circuits of the impedance spectra of these materials are shown in Figure 7. From these impedance spectra we can see that the value of resistance of total arc decreases with increase in Co doping this is due to the good sinter ability of SMCCO with increase in Co content, which ensures it will have good contact between electrode and electrolyte particles.

f. Current Voltage and Current Density: Figure 8 represents the the current- voltage (I-V) and the corresponding power density (I-P) curves for SMCCO operating at pure air at 800°C. the power density increases with increase in Co content. The increased electronic and ionic conductivities and the decreased resistance for the electrode reactions should be responsible for the improved anode performance of Co doped material. The highest power density, obtained for a sample with x=0.7 is 120mWcm^{-2}. After microstructure optimization and electrolyte thickness reduction the performance will be further improved. On the basis of these observations, the $Sr_2Mg_{1\ x}Co_xCrO_{6\ \delta}$ composition is potential anode material for SOFCs.

Conclusion

Double pervoskite oxide of composition $Sr_2Mg_{1\ x}Co_xCrO_{6\ \delta}$ were synthesized by simple sol-gel citrate method. The electrical and ionic conductivity of $Sr_2Mg_{1\ x}Co_xCrO_{6\ \delta}$ was remarkably enhanced by Co doping in the Mg site. The weak Co-O bond is responsible for the increased ionic conductivity, which leads to more oxygen vacancies and lower activation energies for oxygen ion migration. Calcinations temperature has strong impact on the polarization resistance. Co doping can notably enhance the charge-transfer process of SMCCO and thereby decrease the polarization resistance of electrode. SMCCO is potential anode material for SOFCs.

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REFERENCES

Atkinson, A.; Barnett, S.; Gorte, R. J.; Irvine, J. T. S.; Mcevoy, A. J.; Mogensen, M.; Singhal, S. C.; Vohs. “Advanced anodes for high temperature fuel cells”, *J. Nat. Mater*, 2004, 3, 17 27.

Bi, Z. H.; Zhu, J. H.”Effect of Current Collecting materials on the double pervoskite Anode”, *J. Electrochem. Soc.*, 2011, 158, B605 B613.

Brandon, N. P.; Skinner, S.; Steele, B. C. H. Annu. “Recent Advances in Materials for fuel cell”, *Rev. Mater. Res.*, 2003,33,183 213.

Deng, Z. Q.; Zhang, G. G.; Liu, W.; Peng, D. K.; Chen, C. S.,” Germanium and iron co-substituted $SrCoO_{2.5+\delta}$ as oxygen permeable membrane.” *Solid State Ionics*, 2002, 152 153, 735 739.

Fagg, D. P.; Kharton, V. V.; Kovalevsky, A. V.; Viskup, A. P.; Naumovich, E. N.; Frade, J. R.,” The stability and mixed conductivity in La and Fe doped $SrTiO_3$ in the search of potential SOFC anode materials”, *J. Eur. Ceram. Soc.*, 2001, 21, 1831 1835.

Fergus, J. W., “Oxide anode materials for fuel cells”, Solid State Ionics 2006, 177, 1529 1541.

Goodenough, J. B.; Huang, Y. H.,” Alternative anode materials for Solid Oxide Fuel Cells”, *J. Power Sources,* 2007, 173, 1 10.

Haile, S.,” Fuel cells materials and components”, M. Acta Mater 2003, 51, 5981 6000.

Huang, Y. H.; Dass, R. I.; Denyszyn, J. C.; Goodenough, J. B. “Synthesis and Characterization of $Sr_2MgMO_{6-\delta}$ an anode material for the solid oxide fuel cell”, *J. Electrochem. Soc.*, 2006, 153, A1266 A1272.

Huang, Y. H.; Dass, R. I.; Xing, Z. L.; Goodenough, J. B.,” Double pervoskites as an anode materials for solid oxide fuel cells”, *Science*, 2006,312,254 257.

Huang, Y. H.; Liang, G.; Croft, M.; Lehtimaki, M.; Karppinen, M.; Goodenough, J. B.,” Double pervoskite anode material $Sr_2MgMO_{6-\delta}$ (M=Co, Ni) for solid oxide fuel cells”, *Chem. Mater.*, 2009, 21, 2319 2326.

Hui, S. Q.; Petric, A., “Evaluation of Yttrium-Doped $SrTiO_3$ as an Anode for Solid Oxide Fuel Cells,” *J. Eur. Ceram. Soc.*, 2002, 22, 1673 1681.

Ji, Y.; Huang, Y. H.; Ying, J. R.; Goodenough, J. B.,” Electrochemical performance of La- doped $Sr_2MgMO_{6-\delta}$ in natural gas”, Electrochem. Commun. 2007, 9, 1881 1885.

Jiang, S. P.; Chan, S. H.,” A review of anode materials development in solid oxide fuel cells”, *J. Mater. Sci.*, 2004, 39, 4405 4439.

Li, X.; Zhao, H. L.; Gao, F.; Zhu, Z. M.; Chen, N.; Shen, W. “Synthesis and electrical properties of Co-doped Y0.08Sr0.92TiO3-delta as a potential SOFC anodes,” *Solid State Ionics*, 2008, 179, 1588 1592.

Liu, Q.; Dong, X. H.; Xiao, G. L.; Zhao, F.; Chen, F. L.,” A novel electrode material for symmetrical SOFCs.”, *Adv. Mater.*, 2010, 22, 5478 5482.

Lu, X. C.; Zhu, J. H., “Cu(Pd)-Impregnated La0.75Sr0.25 Cr0.5Mn0.5O3?δ Anodes for Direct Utilization of Methane in SOFC,” *Solid State Ionics*, 2007, 178, 1467 1475.

Marrero-Lopez, D.; Pena-Martínez, J.; Ruiz-Morales, J. C.; Perez-Coll, D.; Aranda, M. A. G.; Nunez, P.,” Synthesis, phase stability and electrical conductivity of $Sr_2MgMO_{6-\delta}$”, *Mater. Res. Bull.*, 2008, 43, 2441 2450.

Mclntosh, S.; Gorte, R, “DirectHydrocarbon Solid Oxide Fuel Cell”,. *J. Chem. Rev.*, 2004, 104, 4845 4866.

Miller, D. N.; Irvine, J. T. S.,” B-Site doping of Lanthanum strontium titanate for Solid Oxide Fuel Cell”, *J. Power Sources*, 2011, 196, 7323 7327.

Minh, N. Q., ”Solid Oxide fuel cell technology- features and applications”, *Solid State Ionics*, 2004, 174, 271 277.

Pena-Martínez, J.; Marrero-Lopez, D.; Ruiz-Morales, J. C.; Savaniu, C.; Nunez, P.; Irvine,”Anodic performance and intermediate temperature fuel cell testing of $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ at Lanthanum Gallate electrolytes”, *J. T. S. Chem. Mater.*, 2006, 18, 1001 1006.

Rodríguez-Carvajal,” Recent Advances in magnetic structure determination by neutron power diffraction”, C. Physica B 1993, 192, 55.

Singh, P.; Minh, N. Q.,” Solid Oxide fuel cell: Technology Status”, *Int. J. Appl. Ceram. Technol.*, 2004, 1, 5 15.

Singhal, S. C., “Solid Oxide fuel cells for stationary, mobile and military applications”, *Solid State Ionics*, 2002, 152 153, 405 410.

Steele, B. C. H.; Heinzel,”Materials for fuel cell technologies”, A. Nature 2001, 414, 345 352.

Sun, C. W.; Stimming, U., “Recent anodes advances in solid oxide fuel cells”, *J. Power Sources,* 2007, 171, 247 260.

Tai, L. W.; Nasrallah, M. M.; Anderson, H. U.; Sparlin, D. M.; Sehlin, S. R.”Structure and electrical properties of $La_{1\ x}Sr_xCo_{1\ y}Fe_yO_3$. Part 1. The system $La_{0.8}Sr_{0.2}Co_{1\ y}$ Fe_yO_3”, *Solid State Ionics*, 1995, 76, 259 271

Tao, S. W.; Irvine, J. T. S.,” A redox stable efficient anode for solid-oxide fuel cells”, Nat. Mater. 2003, 2, 320 323.

Tao, S.; Irvine, J. T. S., ” Discoveries and characterization of novel oxide anodes for solid oxide fuel cells”, *Chem. Rec.* 2004, 4, 83 95.

Vasala, S.; Lehtimaki, M.; Huang, Y. H.; Yamauchi, H.; Goodenough, J. B.; Karppinen, “Degree of order and redox balance in B-site ordered double-perovskite oxides, $Sr_2MMoO_{6\ \delta}$ (M=Mg, Mn, Fe, Co, Ni, Zn)” *M. J. Solid State Chem.*, 2010, 183, 1007 1012.

Wang, Z. M.; Tian, Y.; Li, Y. D., “Direct CH_4 fuel cell using Sr_2FeMoO_6 as an anode material”, *J. Power Sources*, 2011, 196, 6104 6109.

Xie, Z. X.; Zhao, H. L.; Chen, T.; Zhou, X.; Du, Z. H. Synthesis and electrical properties of Al-doped $Sr_2MgMoO_{6-\delta}$ as an anode material for solid oxide fuel cells *Int. J. Hydrogen Energy*, 2011, 36, 7257 7264.

Zhang, P.; Huang, Y. H.; Cheng, J. G.; Mao, Z. Q.; Goodenough, J. B.," Sr_2CoMoO_6 anode for solid oxide fuel cell running on H_2 and CH_4 fuels", *J. Power Sources*, 2011, 196, 1738 1743.

Zhang, L. L.; He, T. M.," Performance of double-perovskite $Sr_{2\;x}Sm_xMgMoO_{6\;\delta}$ as solid-oxide fuel-cell anodes", *J. Power Sources*, 2011, 196, 8352 8359.

Zhu, X. F.; Wang, H. H.; Yang, W. S.," Structural stability and oxygen permeability of cerium lightly doped $BaFeO_{3\;\delta}$ ceramic membranes *Solid State Ionics*, 2006, 177,2917 2921.

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