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2013

Xiao, P., Ge, X., Liu, Z., Wang, J.-Y., & Wang, X. (2014). Sr_{1-x}CaxMoO₃-Gd_{0.2}Ce_{0.8}O_{1.9} as the anode in solid oxide fuel cells: Effects of Mo precipitation. *Journal of Alloys and Compounds*, 587, 326-331.

<https://hdl.handle.net/10356/103914>

<https://doi.org/10.1016/j.jallcom.2013.10.187>

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$\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3\text{--Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ as the anode in solid oxide fuel cells: effects of Mo precipitation

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Abstract

Calcium is incorporated into strontium molybdate to form $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3$ as an electronic conductor for solid oxide fuel cells (SOFCs). Metallic molybdenum was observed with the increasing content of Ca substitution for Sr in $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3$. Rietveld refinement reveals the phase transition from cubic to tetragonal perovskite structure, which implies its decreased thermodynamic stability under reducing conditions with increasing content of Ca. X-ray diffraction (XRD) and differential scanning calorimetry-thermo-gravimetric analysis (DSC-TGA) further prove that this Mo ex-solution is reversible. The electrochemical performances of $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3$ towards H_2 and CH_4 oxidation at 800 °C are examined. The performance is improved in H_2 atmosphere with the introduction of Ca, 330 mW cm^{-2} of $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3\text{--Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (GDC) vs. 280 mW cm^{-2} of $\text{SrMoO}_3\text{--GDC}$, which can be ascribed to the segregated Mo as the additional catalyst. However, carbon deposition is observed after exposure to CH_4 at 800 °C for both $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3\text{--GDC}$ and $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3\text{--GDC}$, in contrast to the absence of carbon on $\text{SrMoO}_3\text{--GDC}$.

Keywords

Solid oxide fuel cells

Strontium molybdate

Calcium doping

Mo segregation

Perovskite

1. Introduction

Solid oxide fuel cells (SOFCs) are highly efficient power generators for direct conversion of chemical energy to electrical energy. The state-of-the-art Ni–YSZ anode has achieved high performance towards H_2 oxidation due to the high catalytic activity of Ni. Unfortunately its negative attributes are also exposed, including low tolerance to hydrocarbons or hydrogen sulphide and poor redox stability [1-4]. The development of nickel-free anode with competitive conductivity and electro-catalytic activity to Ni-YSZ has been pursued by many researchers [5-8]. Among them, $(La_{0.75}Sr_{0.25})_{0.95}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM) [9, 10], Sr_2MMoO_6 (M=Mn, Mg) [11] and $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ [12] achieved high redox stability and resistivity towards hydrocarbons and hydrogen sulfide, but with the compromise of power density especially at intermediate temperature (600 °C ~ 800 °C). Although increased performance could be achieved by wet impregnation of 2 wt.% Ni [13], Pd/CeO₂ [14, 15], the agglomeration of the nanoparticles might happen under long-term operation. It has been proposed that durability can be improved if those impregnated nanoparticles can possess the ability of dissolving in and precipitating out of its host. Self-regenerative M (M=Pd, Pt, Rh, Ru) on perovskite or lanthanum chromite materials were first adopted in automotive emission control and methane reforming [16-19]. In-situ segregated metal nanoparticles on ceramic materials that react regeneratively can be a potential solution to the poor catalytic activity of ceramic anode materials towards H_2 and hydrocarbons oxidation. Successful cases [20-23] have been reported to tailor the properties of materials by doping other elements. A Ru doped lanthanum chromite based ceramic by Barnett et al. [24-26] demonstrated an improved performance due to Ru cluster segregation. Yang et al. [27] also reported a redox reversible anode composed of $Pr_{0.8}Sr_{1.2}(Co, Fe)_{0.8}Nb_{0.2}O_{4+\delta}$ (K-PSCFN), which can be obtained by reducing perovskite structure material $Pr_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Nb_{0.1}O_3$ (P-PSCFN) in H_2 .

Regenerative behaviour was observed and high performance was achieved towards both H₂ and CH₄ oxidation due to the segregated Co-Fe alloy. Recently, a highly conductive ceramic material SrMoO₃ has been reported to be a potential candidate to replace Ni [28]. But further work [29] showed a rather low activity towards CH₄ oxidation without additional Pd infiltration. Considering the difficulty for a sole oxide material to perform as well as Ni cermet, GDC (Ce_{0.8}Gd_{0.2}O_{3-δ}) as a mixed ionic and electronic conductor (MIEC) [30, 31] was infiltrated on SrMoO₃–YSZ compound as the anode for SOFCs in our previous work [32]. Although improved performance has been observed, its application was hindered by its limited catalytic activity at the intermediate temperature range (600 ~ 800 °C).

Herein, we report an anode composed of Ca substituted strontium molybdate Sr_{1-x}Ca_xMoO₃ (x=0.3, 0.5) and GDC for SOFCs. As a potential anode, its performance was investigated in both H₂ and CH₄. By introducing Ca on the A site, it is found for the first time that, Mo nanoparticles can reversibly segregate on the surface of Sr_{1-x}Ca_xMoO₃–GDC and perform as the catalyst. In this study, we analysed the effect of the Mo precipitation and further compared the electrochemical performance of Sr_{1-x}Ca_xMoO₃ with SrMoO₃.

2. Experimental

2.1. Materials synthesis

Sr(NO₃)₂ (ACS reagent, ≥99%), Ca(NO₃)₂•4H₂O (ACS reagent, ≥99%) and (NH₄)₆Mo₇O₂₄•4H₂O (BioUltra, ≥99.0%, Sigma-Aldrich) are used as received from Sigma-Aldrich. Gadolinium doped ceria (GDC, Gd 20 mol.%, TC grade) was purchase from Fuel Cell Materials.

Sr_{1-x}Ca_xMoO₄ (x=0, 0.3, 0.5, SCMO_{ox}) were synthesized via a sol-gel method assisted by citric acid [33, 34] as the chelate reagent. Calculated stoichiometric Sr(NO₃)₂, Ca(NO₃)₂• 4H₂O and

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ were mixed with citric acid with the molar ratio of 1:1.5 (metal ion to citric acid) in distilled water at 90 °C under continuous stirring. After slow evaporation of water, a yellowish gel was formed, which was transferred to an oven for ignition treatment at 300 °C for 2 h. The as-obtained powder was ground in a mortar and then pressed into pellets, sintered at 800 °C for 10 h to form crystalline phase in the formula of $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_4$ (SCMO_{ox}). The SCMO_{ox} powder can be obtained by mild grinding the sintered pellets. $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3$ (SCMO_{re}) was finally synthesized by a further reduction of SCMO_{ox} in pure H_2 at 900 °C.

2.2 Materials characterization

The phase structure of the as-synthesized powder was examined by X-ray diffraction using $\text{Cu K}\alpha$ radiation source (Bruker, Japan). The morphology of the anode was examined on field emission scanning electron microscope (FE-SEM, JEOL, JSM6701F, Japan). Thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC) of $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3$ ($x=0, 0.3, 0.5, \text{SCMO}_{re}$) were conducted at a ramping temperature 15 °C/min (TGA, Perkin Elmer) in air.

2.3 Fuel cell test

The $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_4$ –GDC composite was prepared by dispersing $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_4$ and GDC into iso-propanol, which was then ball-milled for 24 h and dried. Anode paste was prepared by mixing $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_4$ –GDC composite with the ink vehicle (VEH, Fuel Cell Materials). A $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ (LSGM) electrolyte supported cell was used in the study. LSGM powder (Fuel Cell Material, USA) was firstly die pressed into pellets and then sintered at 1450 °C for 5 h. The obtained LSGM disks were polished into thin electrolytes of ~350 μm thickness. Anode paste was painted onto the electrolyte and subsequently sintered at 1150 °C for 2 h with an active area of 0.28 cm^2 . $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF, Sigma-Aldrich) was used as cathode. To

circumvent the possible catalytic activity introduced by Pt paste, Ag paste was used as the current collector for anode. $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3\text{--GDC}$ ($\text{SCMO}_{re}\text{--GDC}$) anodes were finally obtained by in-situ H_2 reduction. After stabilization in H_2 for 2 h, subsequent electrochemical measurements were implemented.

A typical home-made alumina tube was used for single cell test. Fuel cell tests were conducted at 800 °C under atmospheric pressure, with H_2 or CH_4 fed at the rate of 50 sccm in the anode whilst the cathode was exposed to ambient air. Current-voltage-power (I–V–P) curves were recorded by a VersaSTAT-3F (Princeton Applied Research). Electrochemical impedance spectroscopy (EIS) was carried out under open circuit voltage (OCV) in a potentiostatic mode from 100 kHz to 0.1 Hz with an AC amplitude of 10 mV.

3. Results and discussion

3.1 Metal Mo segregation on $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3$ and the structure analysis

Fig. 1 shows the XRD pattern of $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_4$ ($x=0, 0.3, 0.5$). A typical tetragonal Scheelite structure of SrMoO_4 was indexed (JCPDS 08-0482), which implies that SCMO_{ox} can be successfully synthesized at 800 °C in 10 h. However, XRD pattern still displays a minor peak at 25.05°, which can be assigned to (111) plane of strontium carbonate. This is possibly caused by a slight adsorption of CO_2 during sintering, and similar phenomenon was observed for SrTiO_3 synthesis [35]. Upon reduction treatment at 900 °C in H_2 during the synthesis of SCMO_{re} , this impurity phase can be completely eliminated, as confirmed by XRD in Fig. 2. In contrast to Fig. 1a, Fig. 1b and 1c show that the peaks, *e.g.* the (112) peak, gradually shift to higher angle, which implies the successful calcium dissolution into lattice for the 30 mol.% and 50 mol.% substituted strontium molybdate. Besides, as shown in Fig. 1c, the high content of calcium incorporated into

the A site leads to the peak splitting and broadening, possibly caused by the lattice distortion due to the ionic radius aberration, Sr^{2+} (1.44 Å) [36] vs. Ca^{2+} (1.34 Å) [37]. After reduction, SCMO_{re} exhibits a perovskite structure in Fig. 2. With the introduction of Ca into A site, we can also observe a gradual peak shift towards higher angle from SrMoO_3 to $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$, which corresponds to the decreased d-spacing. This evidenced the retention of Ca in the lattice under reducing condition, instead of existing in a secondary phase. Furthermore, when Ca partially replaces Sr on A site to form $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3$ and $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$, a new peak can be indexed at 40.5° in Fig. 2, which corresponds to (110) of metallic Mo (JCPDS 42-1120). Mo precipitation is not outstanding when 30 mol.% Ca substitutes for Sr, while the presence of Mo is significant when the Ca content was further increased to 50 mol.%. The structure analysis by the Rietveld Method was carried out using TOPAS. The experimental and calculated profiles of X-ray diffraction data are presented in Figure. S1 and their refinement parameters are listed in Table I. The profile refinements converge to a good solution in space group Pm3m (221), Pm3m (221) and I4/mcm (140) for SrMoO_3 , $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3$ and $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$ respectively. With increasing content of Ca, the structure transits from cubic to tetragonal perovskite. From the graphs presented in Fig. 3c and d, we can clearly see that the MoO_6 octahedrons tilt along z axis(c direction) when 50 mol.% Ca is substituted for Sr on the A site, which is in contrast to cubic SrMoO_3 and $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3$ (Fig. 3a and b). This tilting is obviously caused by Ca (1.34 Å) replacement of Sr (1.44 Å). Previous analysis of Ru ex-solution and nucleation on lanthanum chromite were focused on the Ru diffusion in reducing condition by tracking the changes of the particle size in the course of time [26]. Later, a DFT study on the regenerative behaviour of $\text{LaFe}_{1-x}\text{M}_x\text{O}_{3-y}$ ($\text{M} = \text{Pd}, \text{Rh}, \text{Pt}$) suggested the significance of oxygen vacancies (Vo) in favor of surface segregation [25, 38]. In our case, metal Mo precipitation could be detected by ex-situ

characterization, *e.g.* SEM after reduction in H_2 in less than 2 h. As shown in Fig. 4a and 4b, we can see the ex-solved Mo nucleates into several tens of nano-meters on the scaffold of $SCMO_{re}$ -GDC for both 30 mol.% and 50 mol.% Ca-substituted strontium molybdate, which is in contrast to $SCMO_{ox}$ -GDC anode before reduction (Fig. 4c). Considering the calculated bond length of Mo-O where Mo-O(1) of 1.9705 Å is shorter than 2.0088 Å of Mo-O(2) along the c direction, this lattice distortion could lead to structural instability. At high temperature in H_2 , $SCMO_{re}$ is not thermodynamic stable compared to the undoped one, which could possibly explain the Mo segregation on the surface.

3.2 Reversibility examination of Mo ex-solution

The segregated Mo nanoparticles tend to aggregate at high temperature. A regenerative anode would be a potential solution to the gradual performance degradation caused by particle agglomeration. To examine the reversibility of Mo segregation, XRD was carried out on $SCMO_{re}$ and $SCMO_{ox}$ powder after alternating treatment in H_2 and air. Fig. 5a exhibits the characteristic peaks of the fresh prepared $Sr_{0.5}Ca_{0.5}MoO_4$. Subsequent reduction of the fresh prepared $Sr_{0.5}Ca_{0.5}MoO_4$ in H_2 leads to the emergence of Mo (110) peak at 40.5° (Fig. 5b). After another oxidation/reduction cycle, $Sr_{0.5}Ca_{0.5}MoO_3$ still retains its perovskite structure as shown in Fig. 5c, which indicates the reversible behaviour of Mo segregation in response to reducing/oxidizing conditions. Similar phenomena were also observed for 30 mol.% Ca substituted strontium molybdate by comparing freshly prepared $Sr_{0.7}Ca_{0.3}MoO_3$ of Fig. 6b with the one in Fig. 6c after one redox cycle. As shown in Fig. 6a and 6d, $Sr_{0.7}Ca_{0.3}MoO_3$ can also be re-oxidized back to its oxidizing state, evidenced by the identical peak positions. The slightly broadened peaks could be ascribed to the decreased crystallinity caused by cyclic redox treatment.

To provide further support for molybdenum's dissolution back into the lattice, DSC-TGA analysis was conducted at the ramping rate of 15 °C/min to 900 °C. In Fig. 7a, the TGA curves show two-stage weight increase, which correspond to two exothermic peaks in DSC plot in red arrows, especially for $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$. Clearly, weight starts to change around 400 °C, indicating the onset point of oxidation of SCMO_{re} to SCMO_{ox} , reaches a saddle point at 600 °C in the case of $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$ and finally settles on a plateau above 800 °C. This behaviour presumably indicates the dissolution of metal Mo back to the lattice, in accordance with the second exothermic peak in DSC plot. However, as known that the melting point of MoO_3 is very low at ~ 795 °C [39], it is possible for molybdenum to escape in the form of MoO_3 after oxidation in air at elevated temperature. To examine that, DSC-TGA curve of commercial MoO_3 is shown in Fig. 7b. A typical endothermic peak emerges at ~800 °C, accompanied by a sharp decrease of weight, due to the sublimation of MoO_3 . This is in good agreement with a previous result [39]. In contrast, no endothermic peak is observed for $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3$ samples (Fig. 7a, albeit the second exothermic peak of sample $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3$ isn't obvious, yet still discernible around 800 °C). Instead, the weight starts to increase at around 400 °C and levels off at 800 °C. By referring to the following reaction:

We have calculated the weight increase of 7.3 wt.% and 7.7 wt.% for the oxidation of $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3$ and $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$. These agree with what we have measured by TGA in Fig. 7a. Based on the analysis above, we can conclude that $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3 (x=0.3, 0.5)$ is oxidized to $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_4 (x=0.3, 0.5)$ from 400 °C to 800 °C through reaction (1). No evidence was found to be supportive for molybdenum sublimation in the form of MoO_3 . Instead, its oxidation and

dissolution back into the lattice can be inferred, demonstrating the reversibility of Mo segregation.

3.3 Anode structure analysis and its electrochemical performance towards H₂ and CH₄

Fig. 4d shows the cross-section view of SCMO_{ox} -GDC electrode after sintering at 1150 °C for 2 h. A porous anode of $\sim 70 \mu\text{m}$ in thickness is well attached to LSGM electrolyte. Unlike previous studies, no buffer layer, *e.g.* LDC [40, 41] or SDC [42, 43] was used between anode and electrolyte in our study. By SEM, no obvious reactions can be discerned along the interface.

To test the effect of Mo on fuel oxidation, polarization curves were recorded at 800 °C on SCMO_{re} -GDC anode. After reduction in H₂ for 2 h to ensure the Mo ex-solution, increased performance towards H₂ oxidation can be obtained for $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$ -GDC compared to SrMoO_3 -GDC, 330 mW cm^{-2} vs. 280 mW cm^{-2} , in accordance with the decreased polarization resistance (R_p) in Fig. 8b, which implies that metal Mo does promote catalytic activity. A previous study reported a Ru doped lanthanum chromite-GDC anode [44]. Its performance tested in hydrogen for 96 h was observed 2 ~ 3 times better than that in hydrogen for 15 min because of the ripening of Ru nanoparticles in the course of time. However, our study showed that Mo ex-solution was much faster and these segregated Mo nanoparticles tend to agglomerate into larger particles of several tens of nano-meters, which possibly is the reason for the limited performance improvement. For methane oxidation at the same temperature, unfortunately no activity towards CH₄ oxidation was observed with a rather low OCV ($\sim 0.8\text{V}$). Carbon deposition can be detected by SEM in the anode of $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$ -GDC in Fig. 9a. In contrast, no carbon was observed in SrMoO_3 -GDC anode (Fig. 9b). This result indicates Mo nanoparticles have certain activity towards C-H bond cleavage.

4. Conclusions

Based on an electronic conductive anode material SrMoO_3 [29], we demonstrated a method for performance improvement by partially substituting Ca for Sr on the A site. The Ca substitution decreased the thermodynamic stability upon reducing conditions, resulting in Mo segregation on the surface. We further confirmed this Mo segregation was reversible in response to reducing and oxidizing conditions. This ex-soluted Molybdenum showed its catalytic activity towards H_2 oxidation and C-H bond breaking. For H_2 oxidation, the performance was improved from 280 mW cm^{-2} to 330 mW cm^{-2} at 800°C when 50 mol.% Ca was incorporated. This study demonstrates for the first time that A-site substitution can also lead to B-site metal ex-solution and it differentiates from the previously reported B-site doped anodes with reversible metal ex-solution on B site, which enlightened a new thought to manipulate B-site through A-site doping.

Acknowledgements

We acknowledge financial support from the academic research fund AcRF tier 1 (M4010888 RG20/09 and M4011020 RG8/12) Ministry of Education, Singapore, competitive research program (2009 NRF-CRP 001-032), National Research Foundation, Singapore. Support by the Singapore National Research Foundation under its Campus for Research Excellence And Technological Enterprise (CREATE) programme is also acknowledged.

References

- [1] J. Liu, S.A. Barnett, *Solid State Ionics* 158 (2003) 11-16.
- [2] D. Mogensén, J.D. Grunwaldt, P.V. Hendriksen, K. Dam-Johansen, J.U. Nielsen, *J. Power Sources* 196 (2010) 25-38.
- [3] L.L. Zheng, X. Wang, L. Zhang, J.-Y. Wang, S.P. Jiang, *Int. J. Hydrogen Energy* 37 (2012) 10299-10310.
- [4] Y. Matsuzaki, I. Yasuda, *Solid State Ionics* 132 (2000) 261-269.
- [5] J.B. Goodenough, Y.-H. Huang, *J. Power Sources* 173 (2007) 1-10.
- [6] S. Park, J.M. Vohs, R.J. Gorte, *Nature* 404 (2000) 265-267.
- [7] P.I. Cowin, C.T.G. Petit, R. Lan, J.T.S. Irvine, S. Tao, *Adv. Energy Mater.* 1 (2011) 314-332.
- [8] A. Atkinson, S. Barnett, R.J. Gorte, J.T.S. Irvine, A.J. McEvoy, M. Mogensén, S.C. Singhal, J. Vohs, *Nat. Mater.* 3 (2004) 17-27.
- [9] S. Tao, J.T.S. Irvine, *Nat. Mater.* 2 (2003) 320-323.
- [10] S.W. Tao, J.T.S. Irvine, J.A. Kilner, *Adv. Mater.* 17 (2005) 1734-1737.
- [11] Y.-H. Huang, R.I. Dass, Z.-L. Xing, J.B. Goodenough, *Science* 312 (2006) 254-257.
- [12] Q. Liu, X. Dong, G. Xiao, F. Zhao, F. Chen, *Adv. Mater.* 22 (2010) 5478-5482.
- [13] G. Xiao, F. Chen, *Electrochem. Commun.* 13 (2011) 57-59.
- [14] G. Kim, M.D. Gross, W. Wang, J.M. Vohs, R.J. Gorte, *J. Electrochem. Soc.* 155 (2008) B360-B366.
- [15] G. Kim, G. Corre, J.T.S. Irvine, J.M. Vohs, R.J. Gorte, *Electrochem. Solid-State Lett.* 11 (2008) B16-B19.
- [16] Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto, N. Hamada, *Nature* 418 (2002) 164-167.
- [17] H. Tanaka, M. Taniguchi, M. Uenishi, N. Kajita, I. Tan, Y. Nishihata, J.i. Mizuki, K. Narita, M. Kimura, K. Kaneko, *Angew. Chem. Int. Ed.* 45 (2006) 5998-6002.
- [18] M.R. Goldwasser, M.E. Rivas, E. Pietri, M.J. Pérez-Zurita, M.L. Cubeiro, L. Gingembre, L. Leclercq, G. Leclercq, *Appl. Catal. A Gen.* 255 (2003) 45-57.
- [19] R.M. Navarro, M.C. Alvarez-Galvan, J.A. Villoria, I.D. González-Jiménez, F. Rosa, J.L.G. Fierro, *Appl. Catal. B Environ.* 73 (2007) 247-258.
- [20] Y. Bu, Q. Zhong, D. Xu, W. Tan, *J. Alloys Compd.* 578 (2013) 60-66.
- [21] N. Jaiswal, D. Kumar, S. Upadhyay, O. Parkash, *J. Alloys Compd.* 577 (2013) 456-462.
- [22] L. Tang, J. Zhai, H. Zhang, X. Yao, *J. Alloys Compd.* 551 (2013) 556-561.
- [23] X.G. Cao, S.P. Jiang, *J. Alloys Compd.* 523 (2012) 127-133.
- [24] Y. Wang, B. Madsen, W. Kobsiriphat, S. Barnett, L. Marks, *Microsc. Microanal.* 13 (2007) 100-101.
- [25] W. Kobsiriphat, B.D. Madsen, Y. Wang, L.D. Marks, S.A. Barnett, *Solid State Ionics* 180 (2009) 257-264.
- [26] B.D. Madsen, W. Kobsiriphat, Y. Wang, L.D. Marks, S.A. Barnett, *J. Power Sources* 166 (2007) 64-67.
- [27] C. Yang, Z. Yang, C. Jin, G. Xiao, F. Chen, M. Han, *Adv. Mater.* 24 (2012) 1439-1443.
- [28] T. Maekawa, K. Kurosaki, H. Muta, M. Uno, S. Yamanaka, *J. Alloys Compd.* 390 (2005) 314-317.
- [29] B.H. Smith, M.D. Gross, *Electrochem. Solid-State Lett.* 14 (2011) B1-B5.
- [30] Y. Liu, F. Wang, B. Chi, J. Pu, L. Jian, S.P. Jiang, *J. Alloys Compd.* 578 (2013) 37-43.

- [31] D.H. Prasad, H.R. Kim, J.S. Park, J.W. Son, B.K. Kim, H.W. Lee, J.H. Lee, *J. Alloys Compd.* 495 (2010) 238-241.
- [32] P. Xiao, X. Ge, L. Zhang, J.-M. Lee, J.-Y. Wang, X. Wang, *Int. J. Hydrogen Energy* 37 (2012) 18349-18356.
- [33] A. Aguadero, D. Pérez-Coll, J.A. Alonso, S.J. Skinner, J. Kilner, *Chem. Mater.* 24 (2012) 2655-2663.
- [34] A. Princivalle, G. Martin, C. Viazzi, C. Guizard, N. Grunbaum, L. Dessemond, *J. Power Sources* 196 (2011) 9238-9245.
- [35] V.R. Calderone, A. Testino, M.T. Buscaglia, M. Bassoli, C. Bottino, M. Viviani, V. Buscaglia, P. Nanni, *Chem. Mater.* 18 (2006) 1627-1633.
- [36] X. Li, H. Zhao, F. Gao, N. Chen, N. Xu, *Electrochem. Commun.* 10 (2008) 1567-1570.
- [37] R. Shannon, *Acta Crystallogr. Sect. A: Found. Crystallogr.* 32 (1976) 751-767.
- [38] I. Hamada, A. Uozumi, Y. Morikawa, A. Yanase, H. Katayama-Yoshida, *J. Am. Chem. Soc.* 133 (2011) 18506-18509.
- [39] S. Vasala, H. Yamauchi, M. Karppinen, *J. Solid State Chem.* 184 (2011) 1312-1317.
- [40] Y.-H. Huang, R.I. Dass, J.C. Denyszyn, J.B. Goodenough, *J. Electrochem. Soc.* 153 (2006) A1266-A1272.
- [41] R. Martínez-Coronado, J.A. Alonso, A. Aguadero, M.T. Fernández-Díaz, *J. Power Sources* 208 (2012) 153-158.
- [42] T. Wei, Q. Zhang, Y.-H. Huang, J.B. Goodenough, *J. Mater. Chem.* 22 (2012) 225-231.
- [43] L. Zhang, Q. Zhou, Q. He, T. He, *J. Power Sources* 195 (2010) 6356-6366.
- [44] W. Kobsiriphat, B.D. Madsen, Y. Wang, M. Shah, L.D. Marks, S.A. Barnett, *J. Electrochem. Soc.* 157 (2010) B279-B284.

Figure Caption

Fig. 1 XRD pattern of (a) SrMoO_4 ; (b) $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_4$; (c) $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_4$

Fig. 2 XRD patterns of (a) SrMoO_3 ; (b) $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3$; (c) $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$

Fig. 3 Structure visualization of (a) and (b) for SrMoO_3 and $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3$ (in cubic $\text{Pm}\bar{3}\text{m}$); (c) and (d) for $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$ (in tetragonal I4/mcm) ((c) and (d) are in view of c direction).

Fig. 4 Morphological graph by FESEM: (a) $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3\text{--GDC}$; (b) $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3\text{--GDC}$; (c) $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_4\text{--GDC}$; (d) SEM image for cross-section view of a single cell

Fig. 5 XRD patterns of (a) fresh prepared $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_4$; (b) $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$ obtained by reducing fresh prepared $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_4$; (c) $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$ obtained after a redox cycle (the cycle to oxidize $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3$ to $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_4$ and then reduce back is denoted as one redox cycle)

Fig. 6 XRD patterns of (a) $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_4$; (b) $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3$; (c) $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_3$ after one redox cycle; (d) re-oxidized $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{MoO}_4$ from (c)

Fig. 7 (a) TGA-DTA curves of $\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_3$ oxidation and the DSC curves are assigned accordingly in colours; (b) MoO_3 TGA in black squares and its DSC in red line (peaks of rising-up denoting exothermic, dropping-down as endothermic, indicated by pink arrows)

Fig. 8 (a) $I\text{--}V\text{--}P$ curves for $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3\text{--GDC}$ $\text{SrMoO}_3\text{--GDC}$ anodes at 800 °C in H_2 ; (b) their corresponding EIS curves

Fig. 9 SEM micrographs of (a) $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{MoO}_3\text{--GDC}$; (b) $\text{SrMoO}_3\text{--GDC}$ after methane treatment