



Short communication

## NiO–ScSZ and Ni<sub>0.9</sub>Mg<sub>0.1</sub>O–ScSZ-based anodes under internal dry reforming of simulated biogas mixtures

Y. Shiratori<sup>a,\*</sup>, K. Sasaki<sup>a,b</sup><sup>a</sup> Department of Mechanical Engineering Science, Faculty of Engineering, Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan<sup>b</sup> Hydrogen Technology Research Center, Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan

## ARTICLE INFO

## Article history:

Received 16 November 2007

Received in revised form 15 January 2008

Accepted 3 March 2008

Available online 8 March 2008

## Keywords:

Solid oxide fuel cell

Biogas

Anode

Dry reforming

Internal reforming

## ABSTRACT

Solid oxide fuel cells (SOFCs) with NiO–ScSZ and Ni<sub>0.9</sub>Mg<sub>0.1</sub>O–ScSZ-based anodes were operated by directly feeding a fuel mixture of CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub> (CH<sub>4</sub> to CO<sub>2</sub> ratio of 3:2). Stable operation under constant current load (200 mA cm<sup>-2</sup>) was achieved with a NiO–ScSZ type anode during 200 h operating hours at 900 °C. Less stable operation occurred with a Ni<sub>0.9</sub>Mg<sub>0.1</sub>O–ScSZ type anode. In the case of SOFC with Ni<sub>0.9</sub>Mg<sub>0.1</sub>O–ScSZ as the anode, the methane reforming activity was higher than that with NiO–ScSZ. This was explained by change in the microstructure promoting reforming reactions. However, the addition of MgO resulted in degradation of electrochemical performance due to increase in ohmic resistance of the anode material during operation.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

Biogas, obtained from biomass metabolized by bacteria under anaerobic conditions, mainly consists of CH<sub>4</sub> and CO<sub>2</sub>. Biogas, which is a low-calorie gas and cannot be used efficiently in the conventional combustion engines as a fuel, is available more efficiently in solid oxide fuel cells (SOFCs) [1]. Since the CH<sub>4</sub> and CO<sub>2</sub> ratio depends on site and season, SOFC performance can be affected as well.

A previous study [2] demonstrated that after reduction of Ni<sub>0.9</sub>Mg<sub>0.1</sub>O and Ni<sub>0.9</sub>Mg<sub>0.095</sub>Al<sub>0.005</sub>O-based catalysts at 900 °C, small particles of Ni with ca. 50 nm in size were formed next to (Ni,Mg)O and MgO, respectively. In the case of NiO, Ni particles were formed and agglomerated resulting in smaller catalyst area in the cermet anodes.

In this study, biogas-fueled SOFCs were operated by directly feeding a fuel mixture of N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> (hereafter called simulated biogas) and the methane consumption rate under operation was measured for both NiO–ScSZ and Ni<sub>0.9</sub>Mg<sub>0.1</sub>O–ScSZ-based anode materials.

### 2. Experimental

NiO (>99.9%, Kanto Chemical, Japan) was used as a standard catalyst for SOFC anode. Mixed oxides, Ni<sub>0.95</sub>Mg<sub>0.05</sub>O and Ni<sub>0.9</sub>Mg<sub>0.1</sub>O, were prepared by a precipitation method using nitrates as starting materials and subsequently calcined at 800 °C for 5 h [2]. BET surface areas of the NiO-based oxide powders after reduction in a flow (100 cm<sup>3</sup> min<sup>-1</sup>) of pure H<sub>2</sub> at 900 °C for 2 h were obtained with High Speed Gas Sorption Analyzer (Quantachrome Instruments, USA).

Electrolyte-supported single cells were fabricated. Cell fabrication procedure has been described in detail in the previous paper [2]. 10 mol% Sc<sub>2</sub>O<sub>3</sub>–1 mol% CeO<sub>2</sub>–ZrO<sub>2</sub> (scandia-stabilized zirconia abbreviated as ScSZ) with a thickness of 200 μm and a diameter of 20 mm (Daiichi Kigenso Kagaku Kogyo, Japan) was selected as an electrolyte plate. A mixture of NiO and ScSZ powders with a weight ratio of 5.6:4.4 (abbreviated as NiO–ScSZ) was applied as a standard anode material. Ni<sub>0.9</sub>Mg<sub>0.1</sub>O–ScSZ-based anode was also tested as one of the promising candidates for internal reforming SOFC. A mixture of (La<sub>0.8</sub>Sr<sub>0.2</sub>)<sub>0.98</sub>MnO<sub>3</sub> (abbreviated as LSM) and ScSZ with a weight ratio of 1:1 was adopted as a cathode functional layer and coarse LSM was applied as a cathode current collector layer [3]. The electrode pastes were deposited on the ScSZ plate via screen printing. Porous anode and cathode with the areas of 8 mm × 8 mm were obtained by sintering the deposited pastes at 1300 °C for 3 h and 1200 °C for 5 h, respectively. Cross-sections of single cells were investigated with a field emission scanning elec-

\* Corresponding author. Tel.: +81 92 802 3094; fax: +81 92 802 3094.  
E-mail address: [y-shira@mech.kyushu-u.ac.jp](mailto:y-shira@mech.kyushu-u.ac.jp) (Y. Shiratori).

tron microscope FESEM-S5200 (Hitachi High-Technologies, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS) for microstructural characterizations.

Experimental setup for electrochemical measurements has been described elsewhere [2]. Porous Pt electrode was applied on the cathode side as a reference electrode. 50 ml min<sup>-1</sup> of dry air was supplied to the cathode compartment, and 25 ml min<sup>-1</sup> of simulated biogas mixed with 25 ml min<sup>-1</sup> of pure N<sub>2</sub> was fed to the anode compartment. Flow rates of the gases were controlled by mass flow controllers (HORIBA-TEC, Japan). Catalytic activities of anode materials based on NiO–ScSZ and Ni<sub>0.9</sub>Mg<sub>0.1</sub>O–ScSZ for the dry reforming of methane at 900 °C were investigated by analyzing exhaust gas with an automatic gas chromatograph GC-20B (Shimazu, Japan). For this experiment, three types of simulated biogases, CH<sub>4</sub> rich (CH<sub>4</sub>:CO<sub>2</sub> = 3:2), equimolar (CH<sub>4</sub>:CO<sub>2</sub> = 1:1) and CO<sub>2</sub> rich (CH<sub>4</sub>:CO<sub>2</sub> = 2:3), were selected as the fuels.

Load current was increased up to 128 mA (corresponding to 200 mA cm<sup>-2</sup>) with the rate of 2.56 mA/20 s and then galvanostatic measurement of terminal voltage was started. Anode-side IR drop (between Pt reference electrode in air (RE) and anode) and anodic overvoltage were continuously measured during galvanostatic measurement by means of current interruption method. These electrochemical measurements were performed by using automatic SOFC testing system (TOYO Corporation, Japan).

### 3. Results and discussion

#### 3.1. Microstructure of cermet anodes

For enhancement of catalytic activity of anode material, we prepared Ni<sub>1-x</sub>Mg<sub>x</sub>O solid solutions by means of wet process which led to nano-sized Ni particles after reduction treatment. The microstructure of the Ni<sub>1-x</sub>Mg<sub>x</sub>O-based catalysts has been discussed in detail elsewhere [2,4]. Surface area of the reduced catalyst increased with increasing MgO content, 0.1, 1.6 and 3.1 m<sup>2</sup> g<sup>-1</sup> for NiO, Ni<sub>0.95</sub>Mg<sub>0.05</sub>O and Ni<sub>0.9</sub>Mg<sub>0.1</sub>O, respectively. The addition of MgO was found to be effective in giving larger catalyst area. According to FESEM-EDS analysis, the addition of MgO led to formation of small Ni particles with average size of 50–100 nm and the number of small Ni particles increased with increasing MgO content [4]. Mg uniformly distributed on the Ni catalyst which would contribute to increase in surface area of reforming catalyst.

#### 3.2. Methane consumption rate

CH<sub>4</sub> in biogas mixture is reformed to H<sub>2</sub> and CO mainly through CO<sub>2</sub> reforming reaction on Ni catalysts dispersed in cermet anodes [5–8]. After 50 h operation of biogas-fueled SOFCs at 900 °C under 200 mA cm<sup>-2</sup>, exhaust gases from the anode compartment were analyzed by gas chromatography. Here, electrochemical oxygen supply from cathode to anode,  $v_{O_2}$ , is 1 μmol s<sup>-1</sup> cm<sup>-2</sup> which corresponds to load current of 200 mA cm<sup>-2</sup>. Methane consumption

rates,  $v_{CH_4}$ , obtained by gas chromatography were summarized in Table 1. The values for closed circuit condition reflect the sum of the catalytic and electrocatalytic consumption rate of CH<sub>4</sub>. The higher values for closed circuit condition than those for open circuit condition indicates that during cell operation oxygen on the cathode side transports to the anode side via solid electrolyte and reacts with carbonaceous species derived from CH<sub>4</sub> on Ni-based catalysts. For both NiO–ScSZ and Ni<sub>0.9</sub>Mg<sub>0.1</sub>O–ScSZ,  $\Delta v_{CH_4}$  values ( $v_{CH_4}$  (closed circuit) –  $v_{CH_4}$  (open circuit)) were zero for CO<sub>2</sub>-rich biogas and increased with increasing CH<sub>4</sub> to CO<sub>2</sub> ratio and approached to  $v_{O_2}$ . Similar phenomenon has been reported by Yentekakis et al. [9] for internal steam reforming of methane. They demonstrated that under fuel cell operation at rather high temperature of 900 °C internal reforming was accompanied by electrocatalytic consumption of methane leading to synthesis gas formation (reaction (1)) and  $\Delta v_{CH_4}$  corresponded exactly to  $v_{O_2}$ .



Interestingly, this phenomenon has been observed especially for high CH<sub>4</sub> to H<sub>2</sub>O ratio larger than about 1.5. Also, in the present case, at CH<sub>4</sub> to CO<sub>2</sub> ratio of larger than 1, reaction (1) was found to contribute to anodic reaction whereas at CH<sub>4</sub>:CO<sub>2</sub> = 2:3, the oxygen transported from cathode side during fuel cell operation was totally consumed for the electrochemical oxidation of H<sub>2</sub> and CO.

CH<sub>4</sub> consumption rate increased in the order of supplying CH<sub>4</sub>:CO<sub>2</sub> = 2:3 < CH<sub>4</sub>:CO<sub>2</sub> = 3:2 < CH<sub>4</sub>:CO<sub>2</sub> = 1:1. This result was consistent with that reported by Yentekakis and co-workers [6,7] and indicates competitive adsorption of CH<sub>4</sub> and CO<sub>2</sub> on the Ni catalyst. Since dissociation of CO<sub>2</sub> is considered to be rate-determining step [8], activated carbonaceous species would be derived mainly from CH<sub>4</sub>. Therefore, CH<sub>4</sub>-rich biogas mixture (CH<sub>4</sub>:CO<sub>2</sub> = 3:2) having excess amount of CH<sub>4</sub> would lead to higher amount of carbonaceous species compared to CO<sub>2</sub> rich and equimolar gases. According to thermochemical calculations, compositions of CH<sub>4</sub> rich and equimolar gases were located on the carbon deposition region in carbon–hydrogen–oxygen (C–H–O) ternary diagram [10] (see Fig. 1). This indicates that CH<sub>4</sub> rich and equimolar gases would lead to active carbon species on the catalyst surface which can be electrochemically oxidized during fuel cell operation. These may explain the monotonous increase in  $\Delta v_{CH_4}$  with CH<sub>4</sub> to CO<sub>2</sub> ratio. The larger  $\Delta v_{CH_4}$  for Ni<sub>0.9</sub>Mg<sub>0.1</sub>O–ScSZ than that for NiO–ScSZ indicates that reaction (1) is more promoted on small Ni particles dispersed on the Mg containing oxide support than on coarse Ni in conventional Ni–ScSZ cermet [2,4].

As described in Fig. 1, the CO<sub>2</sub>-rich biogas might be advantageous for preventing carbon deposition. However it is considered to lower electromotive force of biogas-fueled SOFC. As listed in Table 2, open circuit voltage (OCV) decreased with decreasing CH<sub>4</sub> to CO<sub>2</sub> ratio. The values for CO<sub>2</sub> rich gas were at least about 100 mV lower compared to CH<sub>4</sub> rich and equimolar cases. Anodic overvoltages  $\eta$  (IR free) at 200 mA cm<sup>-2</sup> measured by current interruption method were also listed in Table 2.  $\eta$  increased with increasing

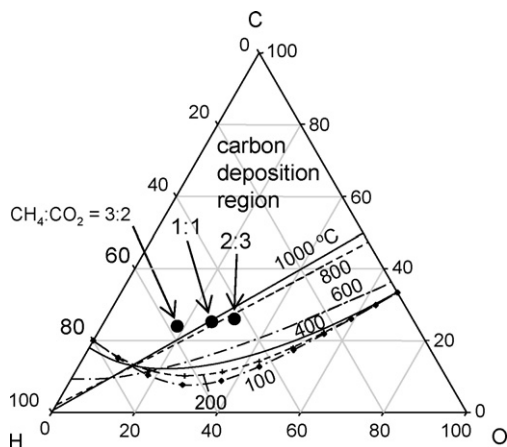
**Table 1**

Methane consumption rate at 900 °C for biogas-fueled SOFC using different types of anode materials under open and closed circuit (200 mA cm<sup>-2</sup>) conditions

| CH <sub>4</sub> :CO <sub>2</sub> | Methane consumption rate $v_{CH_4}$ <sup>a</sup> (μmol s <sup>-1</sup> cm <sup>-2</sup> ) |                     |                                |  |                     |                                |
|----------------------------------|---|---------------------|--------------------------------|--|---------------------|--------------------------------|
|                                  | NiO–ScSZ  |                     |                                | Ni <sub>0.9</sub> Mg <sub>0.1</sub> O–ScSZ |                     |                                |
|                                  | $v_{CH_4}$ (open)   | $v_{CH_4}$ (closed) | $\Delta v_{CH_4}$ <sup>b</sup> | $v_{CH_4}$ (open)                          | $v_{CH_4}$ (closed) | $\Delta v_{CH_4}$ <sup>b</sup> |
| 3:2 (CH <sub>4</sub> rich)       | 5.9   | 6.5                 | 0.6                            | 5.9  | 7.2                 | 1.3                            |
| 1:1 (equimolar)                  | 6.6   | 6.8                 | 0.2                            | 7.3  | 7.6                 | 0.3                            |
| 2:3 (CO <sub>2</sub> rich)       | 3.9   | 3.9                 | 0                              | 5.3  | 5.3                 | 0                              |

<sup>a</sup> Measured by automatic gas chromatograph GC-20B (Shimazu, Japan) after 50 h cell operation.

<sup>b</sup>  $v_{CH_4}$  (closed) –  $v_{CH_4}$  (open).



**Fig. 1.** Positions of three types of simulated biogas ( $\text{CH}_4:\text{CO}_2 = 3:2$ ,  $1:1$  and  $2:3$ ) in the carbon–hydrogen–oxygen (C–H–O) ternary diagram. The limit lines of carbon deposition region at various temperatures were thermochemically calculated by HSC5.1 software (Outokumpu Research Oy, Finland) [10].

$\text{CH}_4$  to  $\text{CO}_2$  ratio. The larger  $\eta$  for  $\text{CH}_4$ -rich biogas mixture corresponded to larger  $\Delta v_{\text{CH}_4}$ . This means that the contribution of reaction (1) would result in larger anodic overvoltage. As shown in Tables 1 and 2, methane consumption rate increased and anodic overvoltage decreased by the addition of MgO to Ni catalyst. The results suggest that the addition of MgO leading to the microstructural change promoted not only reforming reactions but also electrochemical reactions.

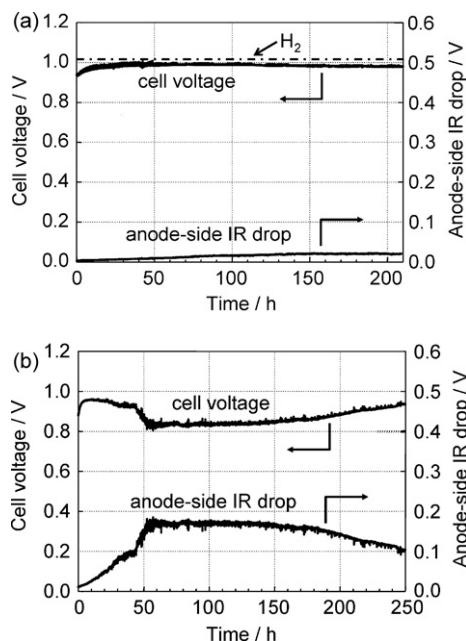
### 3.3. Operation of simulated biogas-fueled SOFC

Time dependences of cell voltage and anode-side IR drop in supplying simulated biogas ( $\text{CH}_4:\text{CO}_2 = 3:2$ ) were shown in Fig. 2. The left and right axes correspond to cell voltage and IR drop, respectively. The measurements were performed at  $900^\circ\text{C}$  for both (a) NiO–ScSZ and (b)  $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ –ScSZ under constant current density of  $200\text{ mA cm}^{-2}$ . In Fig. 2(a), cell voltage of single cell with NiO–ScSZ in supplying  $\text{H}_2$  was also plotted as a dash-dotted line. When NiO–ScSZ is applied as an anode material, direct supply of simulated biogas brought about sufficiently stable and rather high voltage comparable with the case of hydrogen within 200 h operation. When  $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ –ScSZ was used, rapid degradation occurred in the first 50 h. This is due to the increase in anode-side IR drop probably resulting from re-oxidation of reduced catalysts based on  $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ . Through several measurements it was confirmed that  $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ –ScSZ-based anode exhibited relatively larger IR drop compared to NiO–ScSZ-based anode when biogas mixture was fed as a fuel [11]. Fig. 2(b) is an example showing degradation caused by increase in anode-side ohmic loss when  $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ –ScSZ is selected as an anode material. Nevertheless, cell voltage gradually recovered and the voltage at 250 h was higher than the initial cell voltage. Although carbon deposition was thermochemically predicted under the present condition, after operation, carbon

**Table 2**

Open circuit voltages (OCVs) and anodic overvoltages  $\eta$  (IR free) after 50 h operation of biogas-fueled SOFC at  $900^\circ\text{C}$  under  $200\text{ mA cm}^{-2}$  using different types of anode materials

| $\text{CH}_4:\text{CO}_2$ | NiO–ScSZ |             | $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ –ScSZ |             |
|---------------------------|----------|-------------|--|-------------|
|                           | OCV (mV) | $\eta$ (mV) | OCV (mV)                                       | $\eta$ (mV) |
| 3:2 ( $\text{CH}_4$ rich) | 1073     | 81          | 1095   | 59          |
| 1:1 (equimolar)           | 1048     | 61          | 1065   | 46          |
| 2:3 ( $\text{CO}_2$ rich) | 968      | 39          | 968  | 25          |



**Fig. 2.** Time dependence of cell voltage and anode-side IR drop under the constant current density of  $200\text{ mA cm}^{-2}$  measured at  $900^\circ\text{C}$  showing the performance of direct-biogas SOFC with (a) NiO–ScSZ and (b)  $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ –ScSZ. Simulated biogas with the ratio of  $\text{CH}_4:\text{CO}_2 = 3:2$  was fed as a fuel.

deposition was not visible on both anode materials and subsequent EDS analysis could not detect the signal of carbon on the catalyst surface. This result suggests that, applying a certain load current, stable operation of SOFC could be possible even if the mixture of  $\text{CH}_4$  and  $\text{CO}_2$  is directly fed as a fuel, that is, internal dry reforming of methane would be applicable instead of steam reforming. Although, as mentioned in Section 3.2, MgO addition to Ni catalyst brought about higher catalytic activity for internal dry reforming, negative influence by this addition is not negligible. Low conductive Mg-containing oxide phases in the catalyst, MgO or  $(\text{Ni},\text{Mg})\text{O}$  solid solution, cause large ohmic resistance of anode material. As a result, conventional NiO–ScSZ-based cermet anode led to more stable operation than  $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ –ScSZ as shown in Fig. 2. In order to reduce the negative impact on the SOFC operation, electrical property and phase stability of  $\text{Ni}_{1-x}\text{Mg}_x\text{O}$  catalyst in supplying the mixture of  $\text{CH}_4$  and  $\text{CO}_2$  must be systematically investigated.

## 4. Conclusions

SOFCs with NiO–ScSZ and  $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ –ScSZ-based anodes were operated by directly feeding a fuel mixture of  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{N}_2$ . Under  $\text{CH}_4/\text{CO}_2 > 1$ , electrocatalytic consumption of methane was found to occur whereas at  $\text{CH}_4:\text{CO}_2 = 2:3$  the oxygen transported from cathode side during fuel cell operation was totally consumed for the electrochemical oxidation of  $\text{H}_2$  and  $\text{CO}$ . In supplying  $\text{CH}_4$  rich gas ( $\text{CH}_4:\text{CO}_2 = 3:2$ ), stable operation under constant current load ( $200\text{ mA cm}^{-2}$ ) was achieved with a NiO–ScSZ type anode during 200 h operating hours at  $900^\circ\text{C}$ . Less stable operation occurred with a  $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ –ScSZ type anode. In both cases, no carbon deposition was found, despite the fact that under the given experimental conditions carbon was thermodynamically stable. In the case of SOFC with  $\text{Ni}_{0.9}\text{Mg}_{0.1}\text{O}$ –ScSZ, the methane reforming activity was higher than that with NiO–ScSZ. This was explained by change in the microstructure promoting reforming reactions. However, the addition of MgO resulted in degradation of electrochemical performance due to increase in ohmic resistance of the anode material

during operation. In these experiments, small button cells with the electrode area and thickness of  $0.64\text{ cm}^2$  and about  $50\ \mu\text{m}$ , respectively, were used. Therefore, more stable operation could be expected for larger cells or anode-supported cells having larger amount of reforming catalysts.

### Acknowledgement

This work was partially supported by the Ministry of Education, Culture, Sports, Science and Technology, Grant-in-Aid for Young Scientists (B) (19760546).

### References

[1] J. Staniforth, K. Kendall, *J. Power Sources* 71 (1998) 275–277.

- [2] Y. Shiratori, Y. Teraoka, K. Sasaki, *Solid State Ionics* 177 (2006) 1371–1380.
- [3] A.C. Haanappel, J. Mertens, D. Rutenbeck, C. Tropartz, W. Herzhof, D. Sebold, F. Tietz, *J. Power Sources* 141 (2005) 216–226.
- [4] Y. Shiratori, K. Sasaki, *ECS Trans.* 7 (1) (2007) 1701–1710.
- [5] D.J. Moon, J.W. Ryu, *Catal. Today* 87 (2003) 255–264.
- [6] G. Goula, V. Kioussis, L. Nalbandian, I.V. Yentekakis, *Solid State Ionics* 177 (2006) 2119–2123.
- [7] I.V. Yentekakis, *J. Power Sources* 160 (2006) 422–425.
- [8] M. Wisniewski, A. Boreave, P. Gelin, *Catal. Commun.* 6 (2005) 596–600.
- [9] I.V. Yentekakis, Y. Jiang, S. Neophytides, S. Bebelis, C.G. Vayenas, *Proceedings of the Second European SOFC Forum*, Oslo, Norway, May 1996, pp. 131–141.
- [10] K. Sasaki, Y. Teraoka, *J. Electrochem. Soc.* 150 (7) (2003) A885–A888.
- [11] Y. Shiratori, Y. Teraoka, K. Sasaki, *Proceedings of the Seventh European SOFC Forum*, Luzern, Switzerland, 2006, p. 94.