

Degradation of SOFC Cell/Stack Performance in Relation to Materials Deterioration

Harumi Yokokawa[†], Teruhisa Horita, Katsuhiko Yamaji, Haruo Kishimoto, and M. E. Brito

National Institute of Advanced Industrial Science and Technology (AIST), Japan

(Received August 5, 2011; Revised September 5, 2011; Accepted September 5, 2011)

ABSTRACT

The characteristic features of solid oxide fuel cells are reviewed from the viewpoint of the thermodynamic variables to be developed inside cells/stacks particularly in terms of gradients of chemical potential, electrical potential and temperature and corresponding flows of air, fuel, electricity and heat. Examples of abrupt destruction of SOFC systems were collected from failures in controlling their steady flows, while continuous degradation was caused by materials behaviors under gradients of chemical potentials during a long operation. The local equilibrium approximation has been adopted in NEDO project on the durability/reliability of SOFC stacks/systems; this makes it possible to examine the thermodynamic stability/reactivity as well as mass transfer under the thermodynamic variable gradients. Major results of the NEDO project are described with a focus on degradation/deterioration of electrolyte and electrode materials.

Key words : Solid oxide fuel cells, Degradation, Deterioration, Durability, Reliability, Local equilibrium approximation, Degradation mechanism

1. Introduction

Durability and reliability of solid oxide fuel cells (SOFCs) have become an important issue in recent years, mainly because recent rapid progress in constructing and operating SOFC systems for small residential houses makes it necessary to confirm whether long life, high efficiency and low cost can be realized simultaneously.¹⁻⁵⁾ SOFC stack performance must be determined in terms of many properties of respective cell components and their compatibility at interfaces and also must depend on various operational conditions such as those distributions of temperature and oxygen potential to be developed inside the SOFC stacks; this leads to complicated degradation features of SOFCs performance.⁶⁻¹²⁾ The following aspects become crucial:

1) Materials selection is made by considering *physicochemical* properties of respective cell components to be given as functions of temperature and oxygen potential. Even so, the *microstructure* to be determined from the fabrication procedure is also an important factor.

2) Cells consist usually of many functional *interfaces* for electrochemical reactions and electrical connection. Most important interface is electrode/electrolyte interfaces.

3) Stack performance degradation appears as a result of deterioration of respective materials themselves together with related effects due to redistributions of *temperature* and *oxygen*

potential inside stacks.

In the present report, those features which can affect the performance degradation are first described with an emphasis on abrupt destruction of systems, deterioration in fabrication and long term durability. In particular, fundamentals associated with durability are described in a general manner. As an example of the investigation on stack degradation, the NEDO projects on durability and reliability of SOFC stacks will be finally described with an emphasis on those features which have been newly found in the NEDO projects.¹³⁾

2. Characteristic Features of Solid Oxide Fuel Cells and their Relation to Degradation

2.1. Reliability of SOFC Systems

The most important features of fabricating and operating SOFCs are derived from the fact that all issues come from the feature that SOFC is based on the *direct* conversion of chemical energy to electricity by essentially one step. This promises that efficiency in SOFCs can be enhanced by eliminating unnecessary losses in conventional *multi-step* conversion systems based on thermal engines. On the other hand, the same feature of the *direct* conversion in a single step leads to more severe situations for materials stability / compatibilities; namely almost all materials issues appear simultaneously in a single process in fuel cells, while in conventional processes, most severe issue can be isolated from others so as to be overcome with an appropriate method. Particularly, solid oxide fuel cells are fabricated at high temperatures 1200-1300°C and operated around 800-900°C under a steep oxygen potential gradient as well as temperature gradient. These features make

[†]Corresponding author : Harumi Yokokawa
E-mail : h-yokokawa@aist.go.jp
Tel : +81-29-861-0568 Fax : +81-29-861-4540

materials issues quite complicated. Without solving such materials issues, one cannot succeed in fabricating and operating SOFCs.

2.2. Failure in System Operation

First, the SOFC systems are considered with respect to failures in controlling harmonized flows among chemicals, electricity and heats. Since SOFCs are energy convertors to generate electricity, SOFCs are thought to be operated continuously and therefore, flows of chemicals (fuel and air), electricity and heats become essential in establishing reliable operations. When failure is taken place in controlling such flows, serious matters take place as follows;

1) Mistakes in adjusting the flow rate of air in the partial oxidation process. When mass flow meter is not adequately maintained, fuels would be supplied in an improper composition. As a result, Ni will be heavily damaged. Similarly, stop of supplying water to reforming process leads to heavy damages on Ni.

2) In some fuel cell designs, combustion gas of unused fuels can be diffused backwards to the anode area and as a result, nickel can be oxidized and the oxygen potential in the vicinity of nickels will be drastically changed to more oxidative side causing other degradations.

3) Stop of supplying air during cell operation. Whenever current is passing through fuel cells, oxygen should be incorporated into electrolyte. When air is not enough supplied, oxygen atoms inside cathode materials will be extracted into electrolyte. This causes seriously damage of oxide cathodes.

4) Electrical shorting. Whenever shorting occurs inside fuel cells, current will be passed until electrochemical reactions will be stopped due to consumption of fuels or depletion of oxygen, leading to a loss of driving forces for shorting current. Since generated electricity is consumed inside cells, heats evolved are equivalent to the combustion heats causing local heating. At the final stage, electrodes will be fatally damaged.

5) Loss of electrical contact. In parallel cells, current through other cells will increase, leading some degradation due to high current density. In series cells, this directly means a death of fuel cells.

6) Gaseous leakage in stacks. This can happen as electrochemical oxygen permeation through dense materials or as gaseous leakage through cracks, pores or degradation of sealing. General feature of gaseous leakage is that leakage increases with temperature. When gaseous leakage leads to the combustion of gases, this leads to enhancement of gaseous leakage causing local heat. This makes it quite difficult to make thermal management inside stacks.

2.3. Chemical Nature of SOFC Materials and its Relation to Strategy for Stack Fabrication

Room temperature fuel cells are based on acidic or basic membrane as electrolyte, whereas the electrolyte of the SOFC consists of rather mild substances as schematically shown in Fig. 1. This makes materials issues in SOFCs quite mild from the chemical point of view. Even so, strong acidic or basic

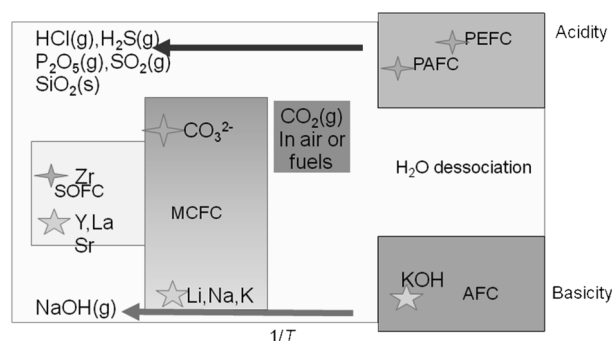


Fig. 1. Schematic drawing to explain the acid-base relation appearing in fuel cell systems such as PEFC, AFC, MCFC and SOFC.

materials are used in other parts of SOFCs and furthermore many acidic and basic substances can be transferred inside the SOFC stacks in the form of gaseous species. In view of this, materials of SOFCs should be carefully selected by considering possible reactions among the materials and with gaseous impurities.

Chemical compatibility among SOFC components is important to keep the interface from being damaged by the formation of third compound or mutual interdiffusion causing the significant composition changes during fabrication process.⁵⁾ Most typical example is the chemical interaction between oxide cathode and electrolyte; that is, the $\text{La}_2\text{Zr}_2\text{O}_7$ formation at the lanthanum strontium manganite (LSM) cathode and yttria stabilized zirconia (YSZ) electrolyte was the critical issue for the first generation. Reactions of the cell components with gaseous species are also important in materials selection. Most famous one is the Cr poisoning on the LSM cathode.⁷⁾ Chromium containing gases will be emitted from the oxide scale of metal interconnect; so this Cr poisoning has to be solved whenever the metal interconnect is used in stacks. These reactions can be well interpreted in terms of valence stability and the stabilization energy of double oxides⁵⁾ or in terms of the acid-base relations.¹²⁾

SOFC designs are categorized by the strategy for overcoming the trade-off relation between the stability and the functionality. The first generation is based and relied on the stability; the LSM cathodes are utilized with the YSZ electrolyte, whereas in the second generations, many attempts are made in adopting more active cathodes such as lanthanum strontium cobaltite (LSC) or lanthanum strontium cobaltite ferrite (LSCF), high ionic conductive electrolyte such as scandia stabilized zirconia (SSZ) or lanthanum strontium gallium magnesium oxide (LSGM) and inexpensive metal interconnects. Critical issues for respective generation cells are summarized in Figs. 2(a) and 2(b). Typical degradation behaviors of the first generation and the second generation are given as flows: For the first generation, Westinghouse/Siemens cells were fabricated with the rather expensive but precise enough electrochemical vapor deposition technique so that the microstructure of electrodes is finely fabricated; degradation was thus quite small from the beginning of development. That is, the voltage degradation

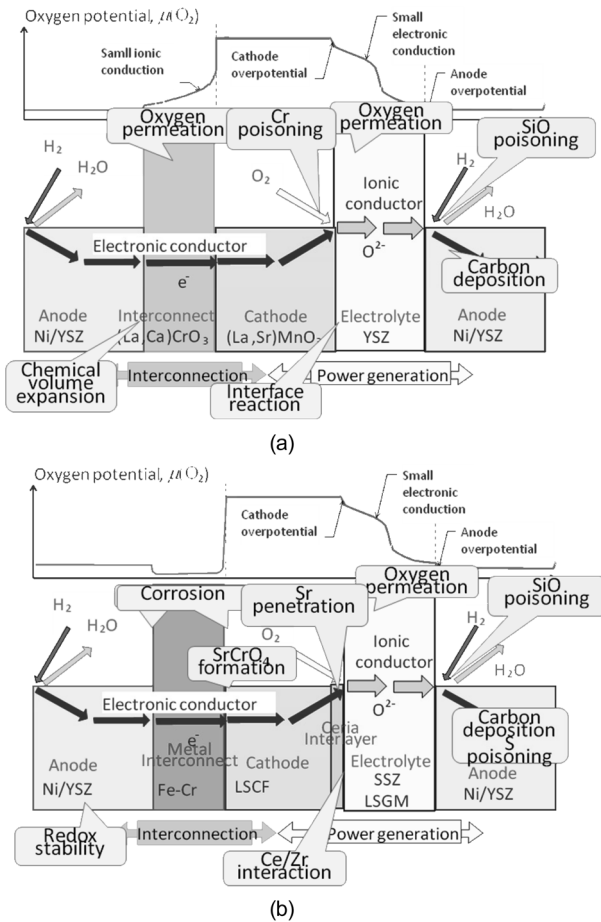


Fig. 2. Schematic drawings for critical issues in materials (a) first generation, (b) second generation.¹⁾

was less than 0.1%/1000 h over 70,000 h operation. As an example of second generation cells, degradation of Sulzer/Hexis system can be considered. This is based on the electrolyte-support cells with metal interconnects and sealant. This system is designed so as to be cost effective. The initial degradation rate was rather high; 50% lowering in voltage occurred around 2000 h and 5000 h for their second generation cells. Even so, improvement was made progressively in recent years and the voltage degradation becomes 1-2%/1000 h or less. In this sense, The second-generation intermediate temperature cells have been well improved by solving many materials problems.

Main issues associated with degradation are summarized in Fig. 3. Since the long term stability of SOFCs is well established for the first generation cells, the main issues for establishment of durability/reliability can be summarized as issues associated with efforts to adopt inexpensive fabrication processes. For the second generation, issues associated with metal interconnects and sealants are crucial. From the physicochemical points of view, both are related with diffusion in solid materials and reactions of cell components with gaseous impurities. Furthermore, stability of complicated structure of cathode-

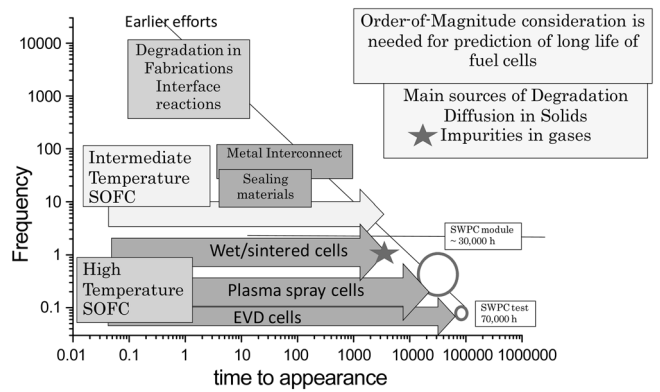


Fig. 3. Schematic plot for number of troubles concerning reliability/durability versus operation time. With improving degradation issues, degradations in a long term appear.

interlayer - electrolyte is also one of sources of degradation; one typical issue is the Sr diffusion through the interlayer and resulting SrZrO₃ formation at the interface between the interlayer and the YSZ electrolyte.

3. Fundamentals of Degradation during Lon-Term Operation: Role of Local Equilibrium Approximation

In order to understand long-term stability of SOFCs, it is essential to know the physicochemical circumstances in which materials are placed and their responses to their changes. To treat such materials behavior, adoption of local equilibrium approximation is essential. This allows to treat mass flows associated with the electrochemical reactions under gradients of thermodynamic variables such as temperature and oxygen potential.

3.1. Heats Evolution and Sink

In Fig. 4, respective heat effects evolving inside cells/stacks are summarized in relation to conversion efficiency and also as locations where those effects take place. The largest contribution should be reversible electrochemical reaction heats

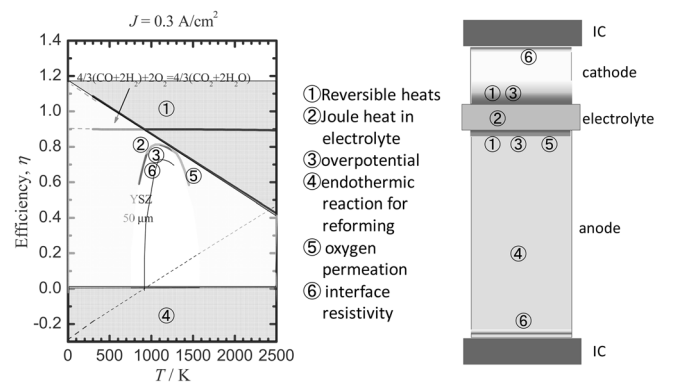


Fig. 4. Efficiency loss and corresponding exothermic effects inside cells/stacks.¹⁾

for selected reactions (for example, oxidation of hydrogen or carbon monoxide). This effect is extensive and therefore changes linearly with current density. The second contribution is related with irreversible effects; Joule heats are linear, while heats due to electrode overpotential are nonlinear. Note that quite a large amount of heats are evolved at the electrochemically active sites as the reversible and the irreversible heats. In this sense, electrode/electrolyte interfaces are crucial points in considering thermally activated degradations.

3.2. Degradation and its Relation to Changes in Distributions of Oxygen Potential, Temperature

The important features of SOFCs are 1) oxygen potential distribution appears inside cells and stacks and this distribution depends on the current density and distribution, and 2) such distribution is in turn affected sensitively by degradations. Fig. 5 shows schematically relation among between electron electrochemical potential, oxide-ion electrochemical potential and the oxygen potential for various cases; that is, (A) under the open circuit voltage (OCV) condition, (B) at a certain current density in the normal state, (C) under the same condition but with thicker electrolyte, (D) for the cathode degraded cell, and finally (E) for weakest cell on shorting among series connected cells. Whenever some anomalous phenomena happen, it is essential to consider under what condition materials are placed; among conditions, oxygen potential is most important.

In Fig. 6, the distribution in the three-phase boundaries is schematically illustrated for Ni anodes, where chemical potentials of hydrogen, oxygen and water are plotted as a function of location under the local equilibrium approximation. Note that the chemical potential of water vapor increases inside of the nickel/electrolyte interface. This consideration can be extended to a system containing H₂S as impurities in fuels.¹⁴⁾

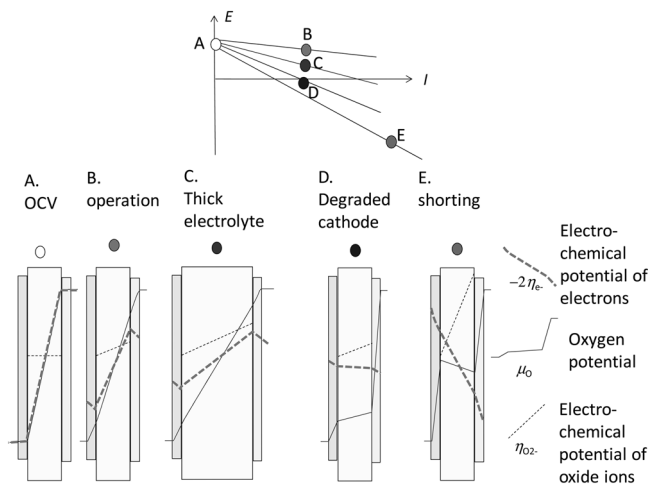


Fig. 5. Schematic distribution of electrochemical potential of electrons, oxygen potential and electrochemical potential of oxide ions. (a) under OCV condition, (b) typical condition at given current density, (c) the same as (b) with thicker electrolyte, (d) cell damaged in cathode, and (e) damaged cell under shorting among several cells.

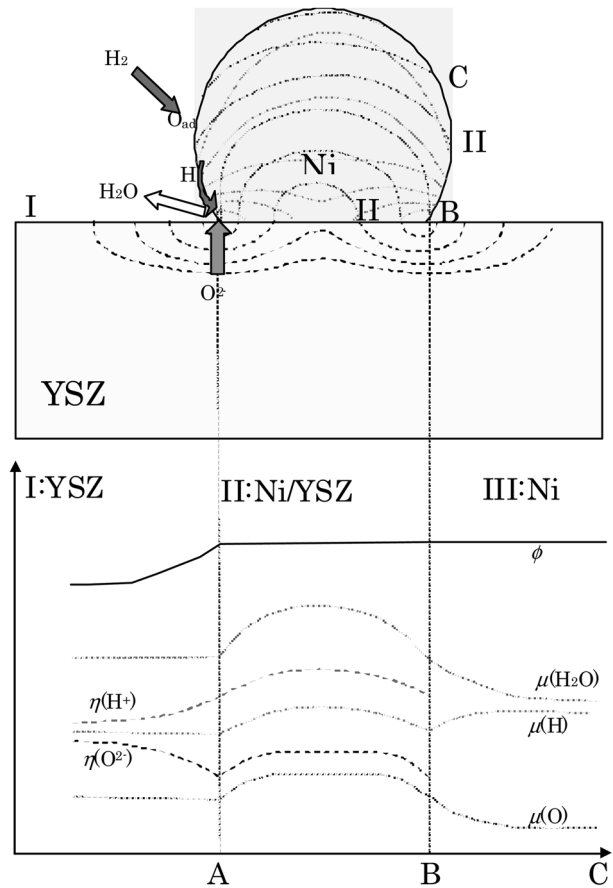


Fig. 6. Local equilibrium approximation in the Ni-YSZ interface; the oxygen potential distribution and related electrochemical or chemical potentials in the vicinity of Ni electrode on YSZ electrolyte.¹³⁾

This suggests that it is quite important to know the oxygen potential distribution around the electrochemically active sites. Note that such a distribution is mainly determined by the electrode reaction mechanism in which active processes are given as functions of current density or temperature. Typically, the three phase boundary (TPB) mechanism and the electrode surface mechanism may provide quite different situation for poisoning effects by impurities. Anyway, at places where the electrochemical reactions take place, the oxygen potential has a steep gradient. In addition to heat effects described above, oxygen potential exhibits also significant change at those sites.

4. NEDO Project on Durability/Reliability

NEDO (New Energy Development Organization) started one three year project on the reliability of SOFCs from 2005FY and continues the project on durability/reliability of SOFC stacks and system from 2008 FY as five year project.¹³⁾ Main focus is to examine the degradation behavior of SOFC stacks as well as cells in cooperation of SOFC developers, public institutes and universities. Main reason why these projects make special focuses on treating stack degradation behavior is based on the

recognition that degradations appearing in button cells which are used widely for degradation investigations may not necessarily be the same as those appearing in stacks. Thus, to know the stack degradation behavior, it is essential to examine directly those stacks which are actually operated in real circumstances.

Main results on the first three-year project can be summarized as follows;¹⁰⁻¹³⁾

1) Long term performance degradations of four stacks (Mitsubishi Heavy Industry (MHI), Kyocera, TOTO and Mitsubishi Materials Corp (MMC)) were in the order of 0.5-1.8%/1000 h. This achievement was rather good and suggests that material selection and adopted fabrication technique provide a certain level of matures in reproducing good performance with less degradation.

2) The presently adopted method of using Secondary Ions Mass Spectrometry (SIMS) to identify the impurity level as a function of operation time successfully provides new information on impurities.⁹⁾ The most interesting result is that contaminated level largely depends on the stacks. Nevertheless, there is no direct relation between the observed performance degradation and the impurity levels, when the degradation level is in the order of 1%/1000 h.

3) Major reason of increasing impurity level during the operation is due to the gaseous species transported within the stream of fuels or air. In this sense, the chemical form of gaseous species becomes critically important when behavior of such elements will be analyzed thermodynamically.

4) Diffusion inside solid materials, on the other hand, was confirmed to be essentially ineffective at the operational temperature. There are, even so, several exceptions such as the Sr diffusion in doped ceria layer and the diffusion associated with oxide scale of metal interconnect. In some cases, nickel shows the sintering or agglomeration due to impurity-enhanced diffusion.

5) Cr poisoning in real SOFC stacks based LSM cathodes was first observed. This is confirmed by the observation of Cr amount concentrated in the TPB area; this time-dependent accumulation is essentially the same as the observed increase

in cathode overpotential.

6) Silica contamination was observed frequently especially in anode side. It is however not easy to find out correlation between the silica amount and the degradation rate.

The second five-year project of NEOO on the durability/reliability started from 2008FT and already spent three years. Main results of the past three year can be summarized as follows;¹³⁾

4.1. Relation of Degradation and Stack Fabrication Sequence

The SOFC stacks consist of ceramic materials so that the high temperature heat treatment is needed for the densification of electrolyte or oxide interconnect. The highest temperature at which respective interfaces will experience during fabrication is one of the important measures for fabrication. Typically, degradation or deterioration of ceramics strongly depends on fabrication temperature. Thus, there can be some correlation between degradation behavior and the fabrication sequence. Table 1 summarizes this correlation. Most impressive results are that cathodes of anode-support cells exhibited some problems associated with degradation, whereas anode itself was very stable; on the other hand, anodes of cathode-support cells or electrolyte support cells exhibited significant sintering.

4.2. Degradation of Electrolyte

The electrical properties of YSZ electrolyte have been well investigated and their aging behavior is commonly observed and interpreted mainly as a result of transformation of the cubic phase to the tetragonal phase.^{15,16)} To identify this transformation, Raman spectroscopy has been utilized on electrolytes of real stacks operated for 5000 h. What was observed in the present study is the location dependent transformation of the cubic to the tetragonal phase.¹⁷⁾ Inside the nickel cermet anode, the tetragonal-phase signal in Raman spectra was most frequently observed and then in the electrolyte located at the interface with the anodes. Interestingly enough, this transformation ceases at the depth of several μm from the Ni/YSZ

Table1. Main Results of Considerations on Possible Correlations between Degraded Parts and Fabrication Sequence

		● issues investigated ○ issues to be improved		◎ issues nearly solved △ issues watched				
	Sequence	Cathode	Electrolyte	anode	IC	con	Status	
IT: flatten tubular (Kyocera, AIST)	Anode-support Electrolyte, IC, cathode	◎ Diffusion					Metals in air; sealant at low temps.	
IT: segment-in-series (Tokyo gas, AIST)	Substrate Anode, electrolyte, IC, cathode	◎ Diffusion					Sealant at low temps; overcome the gaseous leak	
HT: sealless tubular (TOTO)	Cathode-support Electrolyte, IC, Anode		● fuel side	◎	▲		Impurities in fuel sides, No Cr poisoning	
IT: Disk-type (MMC/KEPCO)	Electrolyte-support Anode/cathode, Metall IC	Reactions	△	◎	▲		Sealless; metal IC; impurities in air and fuels	
HT: Segment-in-series (MHI)	Substrate, Anode, electrolyte, IC, cathode	◎ Cr, Diffusion				▲	Crpoisoning; Gaseous leakage	

■ Components to be fabricated with electrolyte

interface. This phenomenon is important when prediction will be made on the aging effect in conductivity of electrolyte, because this transformation speed observed in real stacks is much slower than those observed in the laboratory scale experiments.

Another important observation concerning the YSZ electrolyte is the pulverization of YSZ film of the cathode support cells fabricated with wet sintering method by TOTO.¹⁸⁾ This phenomenon was observed only on the sealless tubular cells fabricated by wet-sintering method. This is apparently due to the significant Mn dissolution into YSZ at higher temperatures. Curiously enough, however, pulverization initiates from the anode side by precipitating manganese oxides. In order to understand this phenomena physicochemically, several tests have been made in TOTO as well as AIST to reproduce the phenomena and to identify plausible effects of other substances. In addition, Tohoku University, a member of the NEDO project, has made investigations on phase relations at lower temperatures near to the operation temperature. Quite recently, better understanding has been achieved on the mechanism and will be published elsewhere.

4.3. Electrodes

1) Generalized models for degradation due to impurities

Anode and cathode activities can be degraded due to the chemical interactions with gaseous impurities. The most important examples are Cr poisoning for cathode, S and other elements in anodes. Although these poisoning features are quite different when different materials for electrode (and sometime electrolyte) are used. Accumulated knowledge can be summarized into the generalized model for electrode-impurity interaction and its relation to the degradation of electrode activities.^{19,20)}

This model considers the following three processes:

1) Electrochemically direct attack of impurities on electrochemically active sites: Typical example of the Cr poisoning on LSM cathodes.

2) Microstructure change due to (impurity-enhanced) diffusion inside electrode materials. Sintering of Ni or cathode is typical.

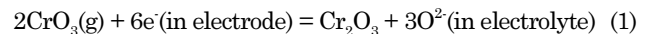
3) Compound formation and trapping effects of impurities on the reacted sites.

In what follows, the first aspect will be focused.

The most important poisoning effect in SOFCs must be the Cr poisoning on the LSM cathode. Whenever the LSM cathode will be used, the Cr evaporation from alloys should be carefully controlled. If this cannot be well managed, other cathodes should be utilized instead of LSM.

In the NEDO project, the Cr poisoning in a real SOFC was first recognized with the aid of precise measurement of Cr concentration in the cathode/electrolyte vicinity with SIMS. It is clarified that several 100 ppm contamination of Cr is enough to give rise to degradation in the order of 1% lowering in performance per 1000 h. Detailed analyses on sources of Cr clarified that this is come from the oxide scale of alloys used for air introduction tube in the test facility. The important fact is that the Cr containing species in the partial pressure of

10^{-10} to 10^{-9} atm is critical to prevent the Cr poisoning. From the SIMS analyses on real stacks as well as button test cells, it is derived that there exists one mechanism by which the Cr containing vapors are selectively deposited on the electrochemically active sites. This is the electrochemical deposition reaction expressed as follows;

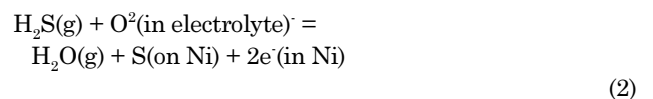


The important point is that during this reaction, electrons in electrode are used, while produced oxide ions are formed in the electrolyte as in the normal electrochemically cathodic reaction.

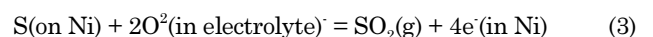
From this finding, we can derive two important features;

1) Similar electrochemical reactions contributed from the electrochemically active species (e^- , O^{2-}) should be taken place at the electrochemically active sites and therefore deposited substances may strongly affect the electrochemical performance. Therefore, degradation behavior should be affected by the properties of deposited substance. For the case of Cr poisoning, Cr_2O_3 does not exhibit good electrode performance so that severe degradation should appear. Note here that during a long period of operation time, the deposited Cr_2O_3 will be dissolved into LSM to establish an equilibrium state; namely, A-site deficient $(\text{La,Sr})_{1-x}(\text{Mn,Cr})\text{O}_3$ is formed initially and followed by $(\text{Mn,Cr})_3\text{O}_4$ precipitation for further Cr-deposition.⁷⁾ Actual performance may depend on such chemical form and microstructure. On contrary, when $\text{PtO}_2(\text{g})$ is transported and deposited,²¹⁾ formed Pt is electrochemically quite active and may cover the intrinsic degradation behavior of cathode materials.

2) A similar mechanism based on the electrochemically cathodic/anodic reactions can be realized even as the volatilization reaction instead of deposition reaction: This will contribute to the recovery from the deposited and poisoned state, if any. Typical reactions are the sulfur poisoning on nickel anodes;



This is the electrochemically poisoning reaction, whereas the recovery process can be written as follows:



It is well known that typical poisoning behavior of Ni anode by H_2S is the initial stepwise lowering in performance followed by the unchanged performance, and this can be recovered after fuel is switched back to the non-contaminated fuel. This behavior can be well interpreted in terms of those competitive nature involved.

Another interesting example is the concentration of phosphor at the nickel cermet anode/electrolyte interface. The poisoning effect of phosphor has been well investigated and severe degradation was observed due to the Ni-P intermetallic compound

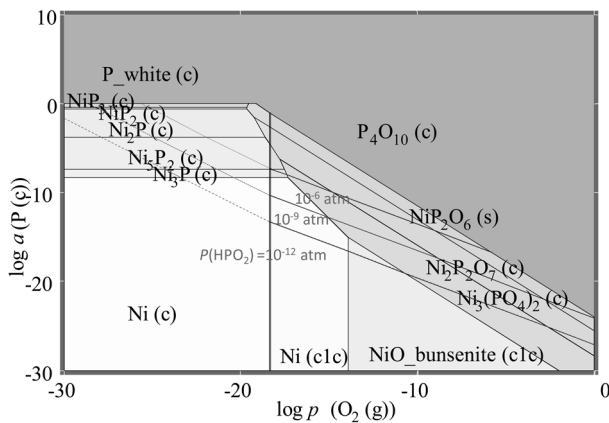


Fig. 7. Chemical potential diagram for the Ni-P-O-H system at 1073 K with a parameter of the partial pressure of $HPO_2(g)$ species.

formation.²²⁾ This strong chemical interaction is consistent with the thermodynamic feature presented in the multicomponent Ellingham diagram.^{12,19)} This implies that almost all phosphor containing gases can be reacted with Ni and other substances in a similar manner of Cr for LSCF cathodes where the $SrCrO_4$ formation is used as trapping mechanism. Interestingly enough, however, the fact that the phosphor concentration was observed at the anode/electrolyte interface indicates that there should be one mechanism which allows the gaseous transportation of the phosphorous component from the reacted Ni-P intermetallic region to the active site. Fig. 7 shows the chemical potential diagram for the Ni-P-O-H system by taking into account of the gaseous HPO_2 species. Thus, the HPO_2 gas in the partial pressure range of 10^{-10} to 10^{-7} atm can be transported through the Nickel anode layer without strong interaction with Ni and reach to the interface, where the nickel phosphate can be formed. Some phosphor can be adsorbed on nickel to enhance Ni agglomeration.

The sulfur contamination exhibits rather complicated behavior to the cell performance. Most heavily contaminated example exhibits a level of 100 ppm observed by SIMS throughout the

Table 2. Dangerous Degree of Impurities in Terms of the Accumulated Amount at Electrochemically Active Sites

Electrode	Concentration in solid detected with SIMS			gases Partial Pres.
	10 ppm	100 ppm	1000 ppm	
sulfur	A	Caution	Danger (whole anode area)	10^{-6} to 10^{-4} atm
phosphor	A	Danger for TPBs		10^{-6} to 10^{-4} atm
Silicon	A	Danger for TPBs		$SiO(g) < 10^{-10}$ atm
Cr	C	Danger for TPBs on LSM		10^{-9} to 10^{-8} atm

anode layer. When compared with other stacks, this level of sulfur contamination is quite high. This anode exhibits various unusual behaviors.

All these considerations on the direct attack on the electrochemical sites can be summarized as the Table 2. Note that the partial pressures of species associated with electrode poisoning are quite low level in the partial pressure. On other wards, only a small number of species is enough to decrease the electrode activity at respective sites.

5. Summaries

As summaries, the followings can be given:

- 1) In order to understand properly the degradation of SOFC cell/stack, it is essential to identify physicochemically the mechanism in cell and stack levels.
- 2) Electrochemical degradation takes place by a change in an extremely tiny scale in a critical region. Materials characterization has to overcome this difficulty by using sophisticated facilities with well developed software for analysis (SIMS, FIB-SEM, simulation).
- 3) Degradation takes place as a result of complicated/combined competitive/sequential processes. When prediction is made for a long term life of the SOFC stacks, such complicated competitive nature should be taken into account properly.

Acknowledgments

Parts of this study were financially supported by NEDO under "SOFC system and elemental technology development."

REFERENCES

1. H. Yokokawa and T. Horita, "Durability, Reliability and Cost Issues from Solid Oxide Fuel Cell Materials Point of View," in Encyclopedia of Sustainability Science and Technology, Springer, to be published
2. H. Yokokawa and N. Sakai, "Part 4. Fuel Cell Principle, Systems and Applications, Chapter 13 History of High Temperature Fuel Cell Development," pp 219-266, in Handbook of Fuel Cells Fundamentals Technology and Application, Vol. 1, Fundamentals and Survey of Systems, Ed. By W. Vielstich, A. Lamm and H. A. Gasteiger, John Wiley & Sons, 2003.
3. H. Yokokawa, "Part 5 Performance and Degradations, Chapter 63 Overview of Solid Oxide Fuel Cell Degradation," pp. 923-932 in Handbook of Fuel Cells Fundamentals Technology and Application, Vol. 6, Advances in Electrocatalyst, Materials, Diagnostics, and Durability, Ed. By W. Vielstich, H. Yokokawa and H. A. Gasteiger, John Wiley & Sons, 2009.
4. H. Yokokawa, H. Tu, B. Iwanschitz, and A. Mai, "Fundamental Mechanism Limiting Solid Oxide Fuel Cell Durability," *J. Power Sources*, **182** 400-12(2008).
5. H. Yokokawa, "Understanding Materials Compatibility," *Annu. Rev. Mater. Res.*, **33** 581-610 (2003).
6. H. Yokokawa, N. Sakai, T. Horita, and K. Yamaji, "Part 5 Performance and Degradations, Chapter 67 Impact of impurities

- on Materials Reliability in SOFC Stack/Modules," pp. 979-991, in Handbook of Fuel Cells Fundamentals Technology and Application, Vol. 6. Advances in Electrocatalyst, Materials, Diagnostics, and Durability, Ed. By W. Vielstich, H. Yokokawa and H. A. Gasteiger, John Wiley & Sons, 2009.
7. H. Yokokawa, T. Horita, N. Sakai, J. Yamaji, M. E. Brito, Y. P. Xiong, and H. Kishimoto, "Thermodynamic considerations on Cr poisoning in SOFC cathodes," *Solid State Ionics*, **177** 3193-98 (2006).
 8. H. Yokokawa, H. Sakai, T. Horita, K. Yamaji, M. E. Brito, and H. Kishimoto, "Thermodynamic and kinetic considerations on degradations in solid oxide fuel cell cathodes," *J. Alloy Comp.*, **452** 41-7 (2008).
 9. K. Yamaji, N. Sakai, H. Kishimoto, T. Horita, M. E. Brito, and H. Yokokawa, "Part 3 Materials for High Temperature Fuel Cells, Chapter 37 Application of SIMS Technique on Durability of SOFC Materials," pp. 555-565, in Handbook of Fuel Cells Fundamentals Technology and Application, Vol. 5, Advances in Electrocatalyst, Materials, Diagnostics, and Durability, Ed. by W. Vielstich, H. Yokokawa and H. A. Gasteiger, John Wiley & Sons, (2009).
 10. T. Horita, H. Kishimoto, K. Yamaji, M. E. Brito, Y. P. Xiong, H. Yokokawa, Y. Hori, and I. Miyauchi, "Effects of impurities on the degradation and long-term stability for solid oxide fuel cells," *J. Power Sources* **193** 194-198 (2009).
 11. H. Yokokawa, T. Horita, K. Yamaji, H. Kishimoto, Y. P. Xiong, and M. E. Brito, "Effect of contamination on the Durability of SOFC Stacks and Modules in Real Operation Condition," Proceedings of 8th European Solid Oxide Fuel Cell Forum, B1004, July 2008.
 12. Harumi Yokokawa, Teruhisa Horita, Katsuhiko Yamaji, Haruo Kishimoto, and Manuel E. Brito, "Materials Chemical Point of View for Durability Issues in Solid Oxide Fuel Cells," *Journal of the Korean Ceramic Society*, **47** [1] 26-38 (2010).
 13. Harumi Yokokawa, "Current Status of NEDO Project on Durability/Reliability of Solid Oxide Fuel Cell Stacks/Systems," *ECS Transactions*, **35** [1] 207-16(2011).
 14. Haruo Kishimoto, Teruhisa Horita, Katsuhiko Yamaji, Manuel E. Brito, Yue-ping Xiong, and Harumi Yokokawa, "Sulfur Poisoning on SOFC Ni Anodes: Thermodynamic Analyses within Local Equilibrium Anode Reaction Model," *J. Electrochem. Soc.*, **157** [6] B802-13 (2010).
 15. For example, S.P.S. Baswal, F. T. Ciacchi, S. Rajendran, J. Drennan, "An investigation of conductivity, microstructure and stability of electrolyte compositions in the system 9 mol% (Sc₂O₃-Y₂O₃)-ZrO₂(Al₂O₃)," *Solid State Ionics*, **109** 167-86 (1998).
 16. For example, M. Hattori, Y. Takeda, Y. Sakaki, A. Nakanishi, S. Ohara, K. Mukai, J-H. Lee, and T. Fukui, "Effect of aging on conductivity of yttria stabilized zirconia," *J. Power Sources*, **126** 23-7 (2004).
 17. Haruo Kishimoto, Taro Shimonosono, Katsuhiko Yamaji, Manuel E. Brito, Teruhisa Horita, and Harumi Yokokawa, "Phase Transformation of Stabilized Zirconia in SOFC Stacks," *ECS Transactions*, **35** [1] 1171-76 (2011).
 18. M. Shimazu, T. Isobe, S. Ando, K. Hiwatashi, A. Ueno, K. Yamaji, H. Kishimoto, H. Yokokawa, A. Nakajima, and K. Okada, "Stability of Sc₂O₃ and CeO₂ co-doped ZrO₂ Electrolyte during the Operation of Solid Oxide Fuel Cells," *Solid State Ionics*, **182** 120-26 (2011).
 19. H. Yokokawa, H. Kishimoto, K. Yamaji and T. Horita, "Generalization of Degradation Mechanisms in terms of Materials Chemical Nature, Operation Condition and Electrode Reaction Mechanisms," pp. 401-410, *SOFC-XI*, Ed. S.C. Singhal and H. Yokokawa, The Electrochem. Soc. Inc., 2009.
 20. Harumi Yokokawa, Katsuhiko Yamaji, M. E. Brito, Haruo Kishimoto, and Teruhisa Horita, "General Considerations on Degradation of SOFC Anodes and Cathodes to Impurities in Gases," *J. Power Sources*, **196** 7070-75 (2011).
 21. YuePing Xiong, Katsuhiko Yamaji, Haruo Kishimoto, Manuel E. Brito, Teruhisa Horita, and Harumi Yokokawa, "Deposition of Platinum Particles at LSM/ScSZ/Air Three-Phase Boundaries Using a Platinum Current Collector," *Electrochem. Solid State Lett.*, **12** [3] B31-3 (2009).
 22. O. A. Marina, C. A. Coyle, E. C. Thomsen, E. D. Edwards, G. W. Coffey, and L. R. Pederson, "Degradation mechanism of SOFC anodes in coal gas containing phosphorus," *Solid State Ionics*, **181** 430-40 (2010).