Development of Toho Gas's SOFC Cells for Durability Improvement

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SOFCs are expected to achieve high electrical conversion efficiency in a wide range of output class, for example CHP systems with small generating power, but an improvement in durability performance is needed for further popularization. Toho Gas aims to commercialize SOFC as a city gas CHP in commercial use. As a part of product development, we are working on ways to prevent physical damage to the SOFC cells and cathode de-lamination. In order to decrease abrasion, it is effective to raise the cathode's firing temperature. However, the electrical performance of cells could decrease if the temperature is too high. Therefore, we need to find an adequate firing temperature that is good for both durability and electrical performance. This paper reports on the relationship amongst the electrical performance, interfacial state, durability performance and firing temperature of SOFC cells (planar type of ScSZ electrolyte supported cell).

Introduction

In Japan, Solid Oxide Fuel Cell (SOFC) Combined Heat and Power (CHP) systems for residential household use have been commercialized since 2011, but cost reduction and improved durability performance are needed for further diffusion. On the other hand, systems for commercial use have been slow in commercializing because of the technical challenges with regard to increased power output.

In a situation like this, there is a movement to accelerate the development of SOFC especially for commercial use in Japan. The New Energy and Industrial Technology Development Organization (NEDO) started a technology demonstration project for commercial use SOFC systems of medium output class (from several kW to several hundred kW) in 2013. Furthermore, the 4th Strategic Energy Plan and the Strategic Road Map for Hydrogen and Fuel Cells have been unveiled by the Government of Japan. These publications highlight the effort to promote the development of SOFC systems for commercial use, and the later publication sets the national goal of bringing SOFC for commercial use to the market at 2017.

Toho Gas Co., Ltd. aims to commercialize SOFC as a city gas CHP for commercial use, and has been developing SOFC cells, stacks and systems since 1990, by manufacturing and evaluating prototype SOFC CHP systems: for example, a 1 kW CHP at the "2005 World Exposition Aichi Japan" and a scale-up 5kW CHP in 2011[1-5].

One of the great challenges for the SOFC industry is durability enhancement. Especially in our case, it is indicated that the primary cause of SOFC degradation is physical damage to cells in long-term operation and the stresses of the thermal cycles, for example, cathode de-lamination due to inadequate adhesive strength. Cathode adhesive strength can be improved by firing the cathode at high temperature in the cell fabrication process, but the electrical performance of the cathode decreases when it was fired at too high of a temperature. This paper reports on the relationship between cell characteristics and cell firing temperature that was evaluated by various methods (electrical performance measurement, interfacial state analysis, and long-term durability measurement), in order to find an adequate firing temperature that is good for both durability and electrical performance.

Experiment

Toho Gas's SOFC cells (Fig. 1) are of electrolyte-supported type. The electrolyte sheet is 10Sc1CeSZ (ZrO_2 stabilized with 10% mol Sc_2O_3 and 1% mol CeO_2). The fabrication process consists of screen-printing of electrode pastes that are a mixture of the raw powder and organic solvents on the electrolyte, and firing in a furnace. As the first firing, NiO-10Sc1CeSZ cermet is printed on one side of the electrolyte sheet for the anode, and GDC is printed on the other side for the interlayer, then the assembly is fired in a furnace. As the second firing, LSCF-GDC is printed on the interlayer for the cathode, and fired.

Firstly, we fabricated small button cells (Φ=14 mm) by firing their cathodes at several temperatures (850 to 1250°C), and narrowed down the adequate firing temperatures to a range of 1000 to 1150°C, which yielded cells that have both good electrical performance and interfacial state, in terms of their electrical performance, adhesive strength and observations of inter-facial microscopic structure.
After this, we fabricated single cells (8.5 x 8.5 cm^2) that were sized for installing onto our stacks, and evaluated the degradation rate in long-term operation. These experiments suggest that the optimal firing temperature zone for our cells, which is good for their electrical performance and durability, has been found.

The power generation performance of the button cells (Φ =14 mm) was evaluated by IV measurement and current interruption method (0.3A/cm^2) at 800°C. The interfacial state between the electrolyte/interlayer/cathode of the cells was investigated by scanning electron microscope (SEM), and an elemental distribution was analyzed by energy dispersive X-ray spectrometry (EDX) attached to our SEM. Furthermore, the adhesive strength of the cathodes was quantitatively evaluated using a micro-scratch tester (CSR-2000; made by RHESCA Co. Ltd., Japan), which is one of the methods for evaluating thin layer adhesive strength. We applied this to our SOFC cells. Finally, the durability of single cells (8.5 x 8.5 cm^2) was evaluated as degradation rates under galvanostatic condition (0.25 A/cm^2) for up to 1000 hours at 800°C.

Results and Discussion

Firstly, electrical performances of the button cells (fired at 850 to 1250°C) were evaluated at 800 °C (Fig. 2). The electric performance of the cells fired at 1100 °C was the highest, while, it was worse for those fired at too low (e.g. 850 °C) or too high (e.g. 1250°C) of a temperature. Furthermore, resistance components R_{ohm} (derived from the electrical resistance of materials) and η/i (derived from the activation energy of reaction and the gas diffusion process in electrodes) were evaluated by current interruption method at 0.3 A/cm^2 (Fig. 3). The former became lower as the firing temperature became high, the latter correlated weakly with the firing temperature, and both were too high when the firing temperature was 1250°C.

This firing temperature dependence of the electric performance of the cells is discussed below with regards to the interfacial state between the electrolyte/interlayer/cathode.

Firstly, the case of 1100°C in which electrical performance was the highest is considered. The cross-section SEM image of the interlayer/cathode interface fired at 1100°C showed a favorable condition with no de-laminated parts at the interface and a porous structure for each layer (Fig. 4). Such a favorable condition was also observed in the case of 1000°C and 1150°C. Furthermore, it was seen that, since the cathode was fired at a higher temperature, the adhesive strength of the cells became higher, and saturated over 1050°C (Fig. 5). This was evaluated before the power-generating operation, so the adhesive strength of the cathode fired at over 1050°C is expected to be efficient at that time.

Secondly, possible causes of the low electric performance from firing at too high of a temperature is considered. From cross-section SEM images, de-laminated parts at the interlayer/cathode interface were observed in the cell fired below 1000°C (Fig. 6, left picture). This result coincides with low adhesive strength at low firing temperature (Fig. 5, below 950°C). The above indicates that inadequate adhesive strength and inadequate formation of the interface between interlayer/cathode fired at low temperature could lead to a high R_{ohm} and inferior electric performance. The above discussion is about cells before the power-generating operation, but we think that such inadequacy in the interface could contribute to de-lamination under long-term operation and thermal cycling, as well.

On the other hand, de-lamination was not observed at the interface fired at 1250°C, but obstruction of the porous structure of each of the layers caused by excessive sintering was observed (Fig. 6, right picture). We think that this obstruction could lead to a decrease in the reaction field, insufficient gas diffusion, and inferior electric performance.

Another phenomenon that occurs when the firing temperature is high is elemental diffusion between layers. EDX analysis showed that Sr contained in the cathode diffused through the interlayer into the electrolyte/interlayer interface when it was fired at over 1150°C, but it was not observed in the cases of cells fired at below 1100°C (Figs. 7 and 8). Sr at the electrolyte/interlayer interface could combine with Zr contained in the electrolyte and oxygen, and form a highly-resistive oxide, which decreases electrical performance.

As such, the prevention of these phenomena must be considered during the cell production process, in order to fabricate them to an adequate interfacial state.

From these evaluations of button cells (fired at 850°C to 1250°C), we determined the promising firing temperatures for cathodes to be a range from 1000°C to 1150°C. Single cells were fabricated at these temperatures, and their durability performance evaluated (Fig. 9). The results of galvanostatic durability tests indicated that single cells fired at 1050°C and 1100°C demonstrated better durability performance than the others, and this tendency was reinforced in retesting (Fig. 9).

However, the electrical performance and durability of cells vary. In addition, degradation factors besides de-lamination were not considered this time and should be the subject of future investigations.

Conclusions

The relationship of electrical performance, interfacial states, durability and firing temperature of planar type ScSZ electrolyte supported cells was investigated. At this time, examination results suggest that the cells fired at 1050°C and 1100°C are adequate for our cathode.

Hereafter, we plan to evaluate electrical performance and durability performance of cells in a condition close to practical usage, for instance, loading cells into our stacks. In addition, we need a clear understanding of de-lamination and a preventive measure for it. One of the possible factors applying tensile stress to the cathode is heat stress between cells and interconnectors induced by mismatched coefficients of thermal expansion. This unpleasant repercussion could be decreased by using interconnectors that have a coefficient of thermal expansion close to our cells or ScSZ. As such, we will aim to improve the durability of SOFC as a system by both process improvement and optimization of usage environment.

References

1. Y. Mizutani, M. Kawai, K, Nomura, Y. Nakamura, and O. Yamamoto, *Solid Oxide Fuel Cells VI*, Ed. by S.C. Singhal and M. Dokiya, PV99-19, p.185, The Electrochemical Society Proceedings Series, Pennington, NJ (1999).
2. K. Ukai, Y. Mizutani, Y. Kume, and O. Yamamoto, *Solid Oxide Fuel Cells VII*, Ed. by H. Yokokawa and S.C. Singhal, PV2001-16, p.375, The Electrochemical Society Proceedings Series, Pennington, NJ (2001).
3. H. Sumi, K. Ukai, K. Hisada, Y. Mizutani and O. Yamamoto, *Sixth European Solid Oxide Fuel Cell Forum Proceedings*, Ed. by M. Mogensen, p.1214, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).
4. Y. Mizutani, K. Hisada, K. Ukai M. Yokoyama, and H. Sumi, *J. Alloys. Compd.*, 408-412, 518 (2005).
5. M, Yokoyama, M. Kawai, K. Nomura, Y. Nakamura and O. Yamamoto, *Solid Oxide Fuel Cells IX*, Ed. by S.C. Singhal, J. Mizusaki, PV2005-07, p.208, The Electrochemical Society Proceedings Series, Pennington, NJ (2005).

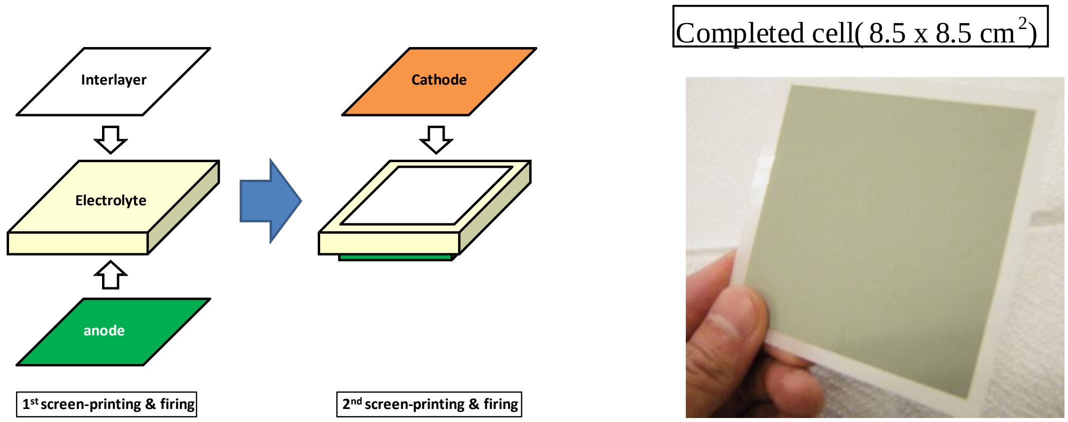

Fig. 1 Fabrication process and photograph of Toho Gas's planar type of ScSZ electrolyte supported cell

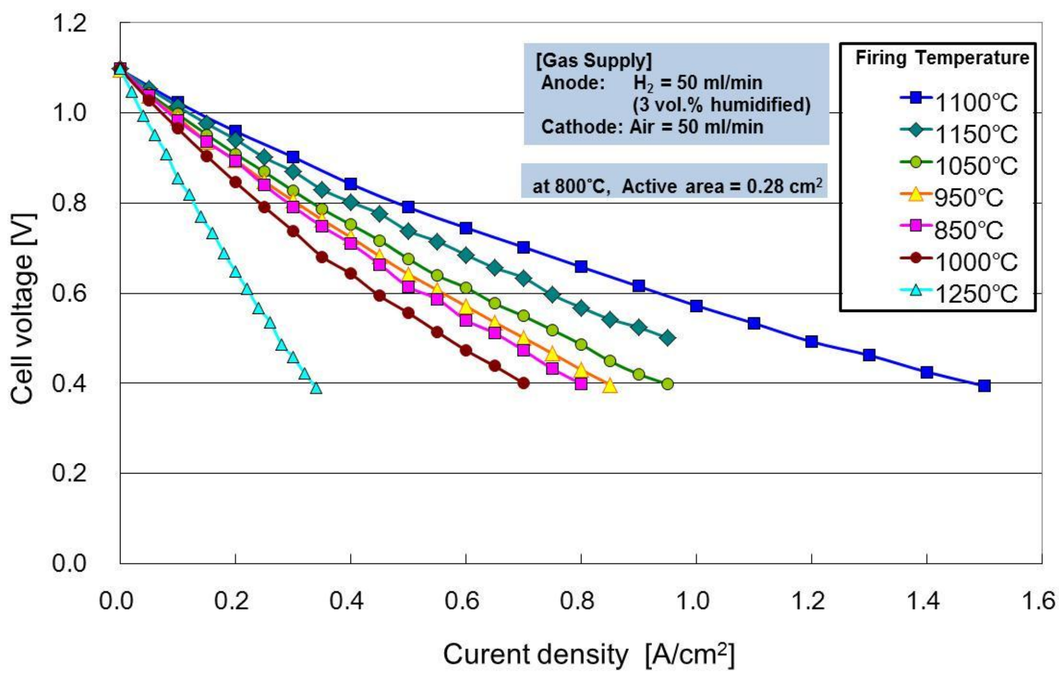

Fig. 2 Relationship between electrical performance of button cells at 800°C and other firing temperatures

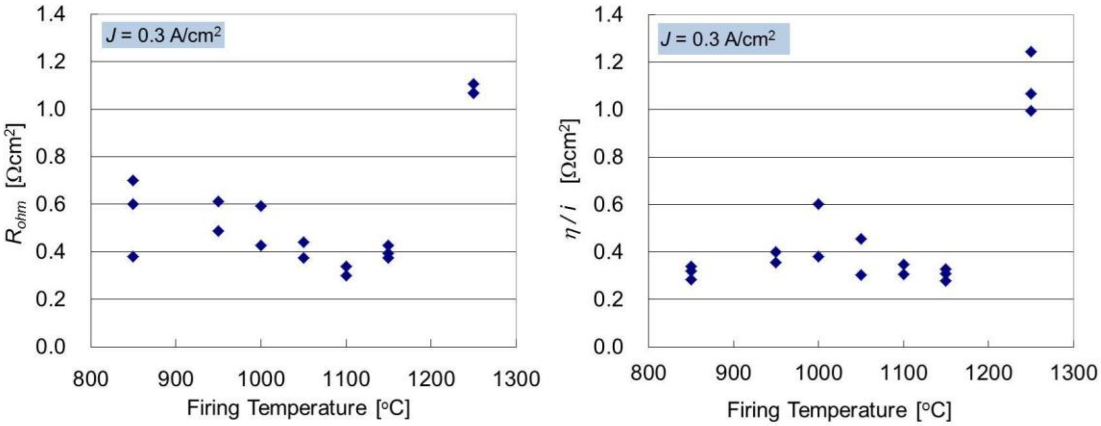

Fig. 3 Relationship between resistance components (left graph: R_{ohm}, right graph: η/i) at 800°C and other firing temperatures

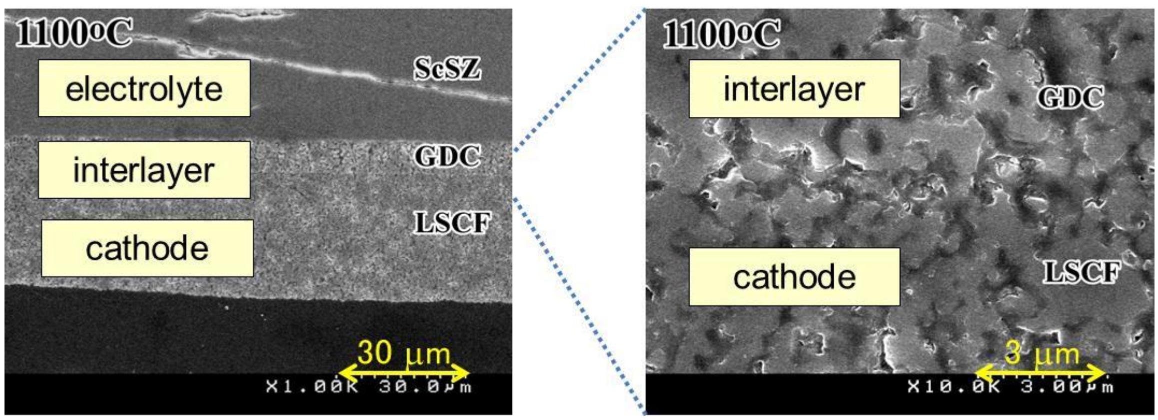

Fig. 4 Cross-section SEM image of electrolyte/interlayer/cathode interface fired at 1100°C

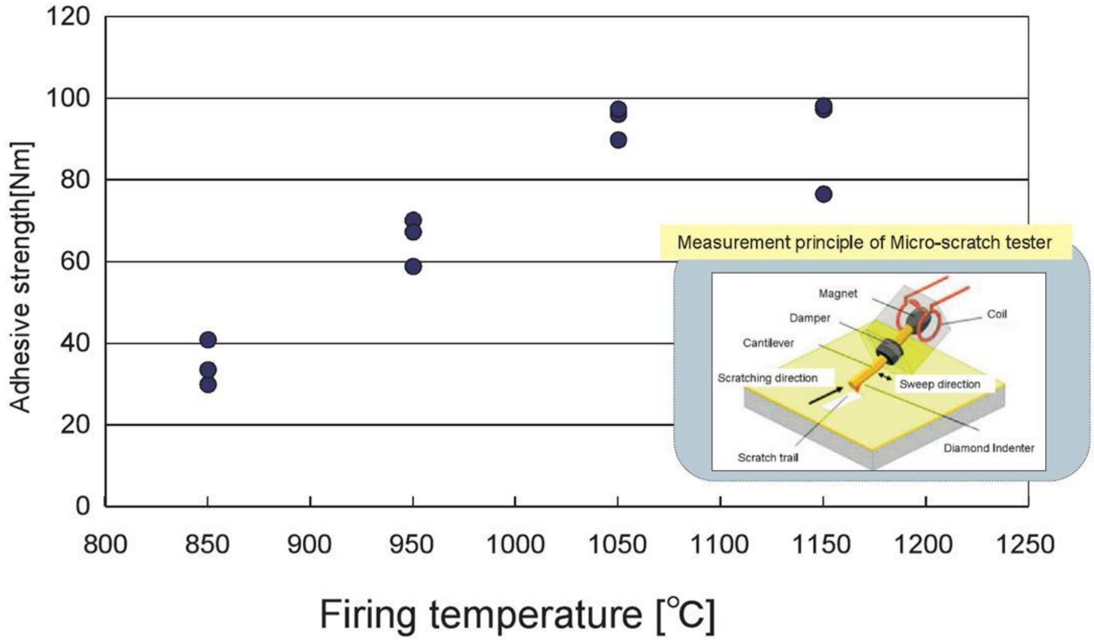

Fig. 5 Relationship between adhesion strength and firing temperature (Using a micro-scratch tester made by RHESCA Co. Ltd.,).

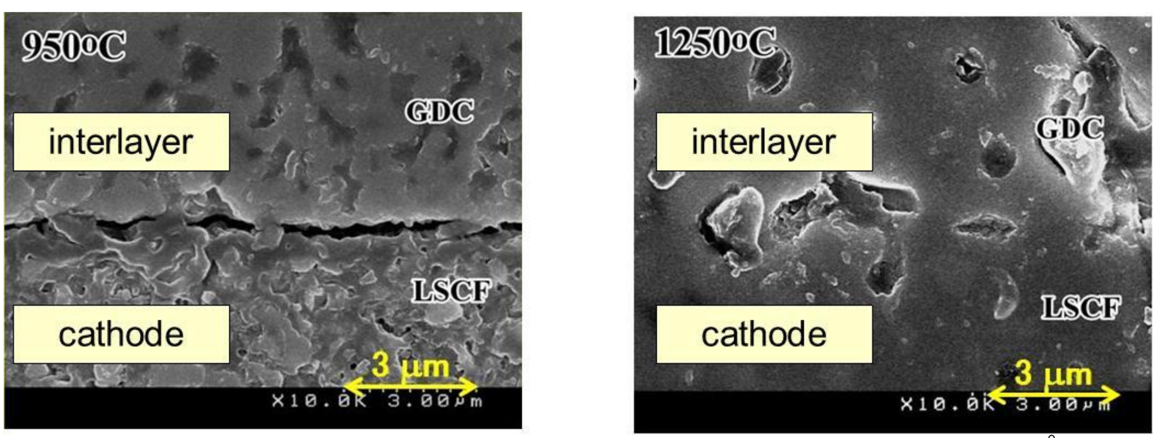

Fig. 6 Cross-section SEM image of interlayer/cathode interface fired at 1100°C (Left picture: De-laminated) and 1250°C (Right picture: Excessive sintering)

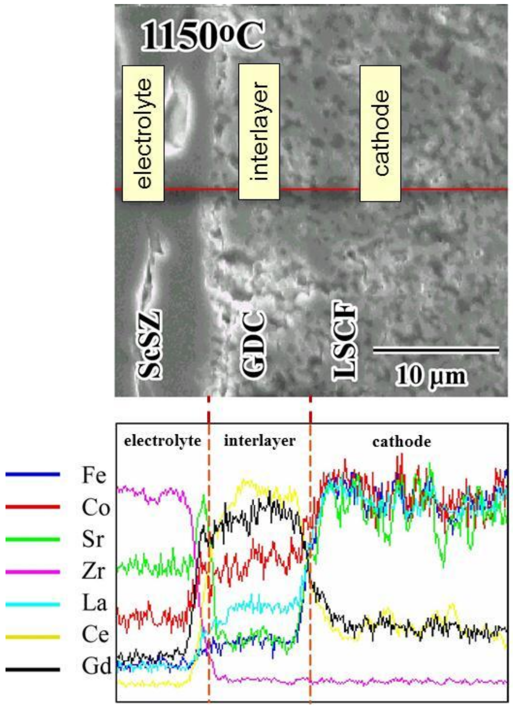

Fig. 7 Cross-section SEM (Above picture) and EDX (Below graph) images of electrolyte/interlayer/cathode interface fired at 1150°C

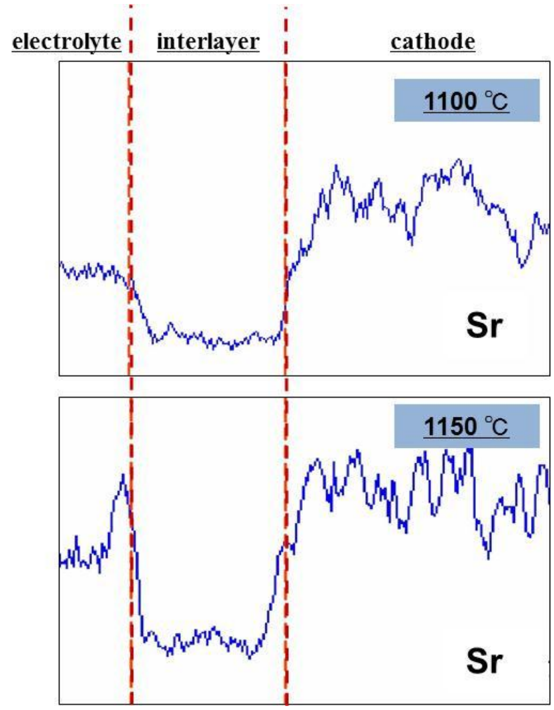

Fig. 8 Distribution of Sr analyzed by EDX at the electrolyte/interlayer/cathode interface fired at 1100°C (Above graph) and 1150°C (Below graph)

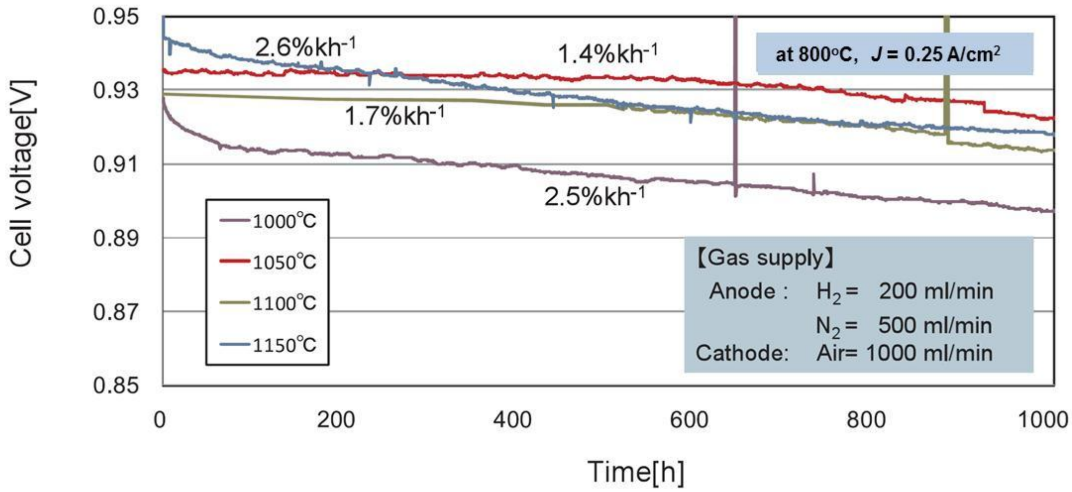

Fig. 9 Galvanostatic durability curves of single cells fired at different temperatures

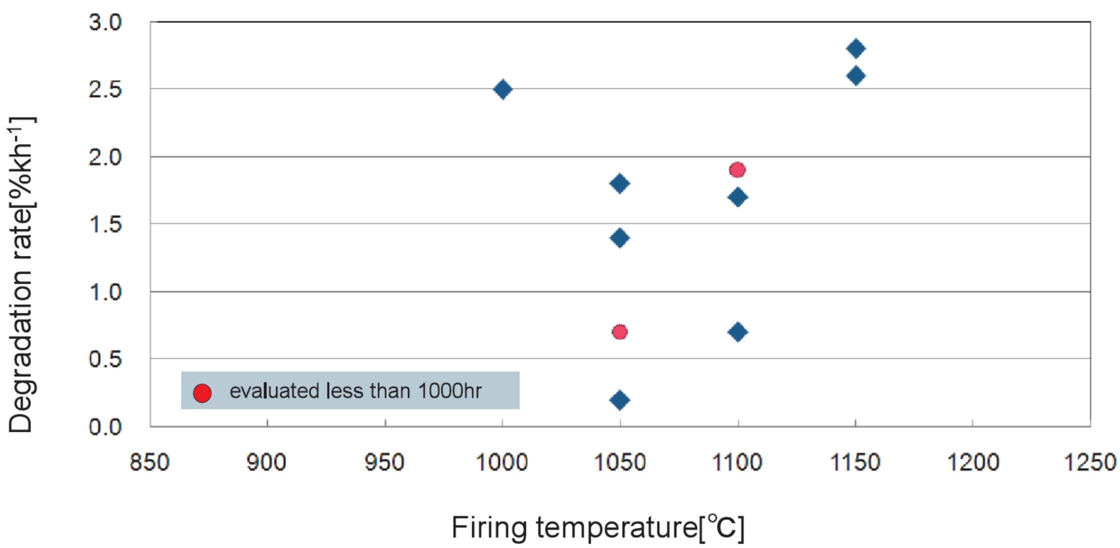

Fig.10 Relationship between degradation rate and cathode firing temperature