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General considerations on degradation of Solid Oxide Fuel Cell anodes and cathodes due to impurities in gases

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ABSTRACT

The degradation mechanism of cathodes and anodes due to gaseous impurities has been considered to provide generalized understanding of materials behavior involved in degradation and hopefully to possible recovery processes. Considerations can be made in terms of (1) the chemical reactivity of gaseous impurities with a main component of electrode materials, (2) diffusivity of main components associated with chemical reactions, and (3) electrochemical reduction/oxidation processes of gaseous impurities in competing with recovery processes due to those electrochemical reactions or chemical reactions which lead to the volatilization of deposited substance and removal of poisons from the electrochemically active sites. The chemical reactivity of the main component with gaseous impurities can be well characterized in terms of the thermodynamic properties such as interaction parameters for intermetallic compounds or the stabilization energy/the valence stability of the transition-metal oxides for oxide electrodes. Diffusivity of main components should be discussed with the enhancement due to surface coverage of impurities. The electrochemical reduction/oxidation of the gaseous impurities provides the mechanism of impurities being deposited and accumulated at the electrochemical reaction sites. Possible recovery process could be examined by whether corresponding electrochemical or chemical process for the deposited substances to be volatilized is available.

1. Introduction

In recent years, there are growing strong interests in applying the solid oxide fuel cells to cogeneration systems for the residential houses [1]. Among the fundamental features of the SOFC systems as energy converters, the durability/reliability, in other words, life time is the most important in the early entry to the markets compared with the rest of the features, efficiency and cost, although the latter two features are also important and their achievement is closely related with the durability/reliability issues [2–10].

We have involved with the NEDO project on the reliability of SOFC stacks/modules conducted from 2005 to 2008 [3–5]. The main topic of this project was to make detailed analyses of cell components after a long term operation with the SIMS (Secondary Ion Mass Spectrometry) technique applied to the real SOFC stack materials. The following four stacks/modules were cooperated: segment in series tubular cell made by Mitsubishi Heavy Industry (H1), Flatted tube cells made by Kyocera (L1), Seal-less tubular cell made by TOTO (H2), and Disk-type planar made by Mitsubishi Materials (L2). The following results were obtained [6]:

(1) It has been well recognized that the SIMS technique [5] can be successfully applied to detect the interdiffusion of elements across interfaces of cell components as well as detect the impurity migration within the SOFC stacks.
(2) Basically cation diffusion across the interfaces during operation is quite small. Exceptions are diffusion in cathode complex layers including ceria interlayers and diffusion in metals/alloys including oxide scales. In some cases, nickel sintering appears to be significant.
(3) Detected chromium deposited in the LSM cathode/YSZ-electrolyte interface is quite limited even though several per cent of performance degradation is observed. This suggests that in order to achieve a long life in the range of 40,000–90,000 h, it becomes essential to carefully control the accumulation of poisoning elements in the electrochemical reaction sites within the contamination level of 1–1000 ppm. For this region, only SIMS can be applied to detect the materials behavior.
(4) In some cases, contamination by impurities becomes significant. At the end of the project, it was not easy to find the

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correlation of impurities and performance degradation which was in the range of 0.8–1.5%/1000 h.

These findings are quite important to improve the stack performance from 1%/1000 h level to 0.25 or 0.1%/1000 h. This also indicates further need to make more fundamental investigations on correlation between the degradation behavior and materials behaviors inside SOFC stacks.

Thus, a new NEDO project has been organized as five-year project from 2008 to 2013. One stack made by Tokyo gas/Kyocera joined newly to the NEDO project. Several university groups participate to clarify the degradation mechanism. There are several aims/strategies adopted in this project as given below:

(1) Various experimental facilities will be combined to observe the materials within stacks. In addition to SIMS, a new machine such as FIB/SEM will be introduced to obtain the microstructures of electrodes.
(2) Common approach: Universities/research institutes share the key concept that those electrochemical processes which are taken in fuel cells should be well described in terms of the local equilibrium approximation. This approximation is an old but fundamental idea for understanding the high temperature corrosion. Mizusaki et al. [11] proposed that the same idea can be well applied to the electrochemical process associated with cathode and anode electrode reaction mechanism. One of the merits of this approach is that understanding the interface chemistry is rather easy to be correlated with the electrochemical behavior; a most interesting example is the $La_2Zr_2O_7$ formation at the LSM/YSZ interface [12]. This can be also applied to sulphur poisoning.

The latter local equilibrium model seems to be powerful in obtaining the common degradation mechanism among various cathodes as well as nickel cermet anodes. In the degradation studies on cathodes, many reactions or elements have been tested. This can be interpreted in terms of thermodynamic stability relations [7,8]. For anodes, thermodynamic analyses have been made to clarify the chemical interaction between Ni and impurities. In recent years, a significant amount of efforts have been made in US to clarify the interactions between nickel and impurities originated from coal based fuels [10]. Since their results are quite interesting from the material chemical point of view with which our interpretation has been tested, attempts have been made to extract the important features from the respective poisoning phenomena, to combine those features to set up a common, well generalized model associated with degradation of electrode by foreign elements, and finally to apply new ideas/mechanism to respective poisoning system again, leading to new insight into the degradations.

2. Interpretation of PNNL/NETL/WVU results

Within the DOE/SECA project, PNNL (Pacific Northwest National Laboratory), NETL (National Energy Technology Laboratory) and WVU (West Virginia University) made intensive and extensive investigations on effects of coal-derived gaseous impurities on nickel-YSZ cermet anodes [10,13–19]. On the other hand, we have calculated and constructed the chemical potential diagrams for the Ni–M–O–H (M = S, Se, As, P) systems [20,21]; for the Ni–P–O–H system, we modified the early diagrams by adopting the thermodynamic data for the HPO_n(g) (n = 1,2,3) as suggested by Bao et al. [22–24].

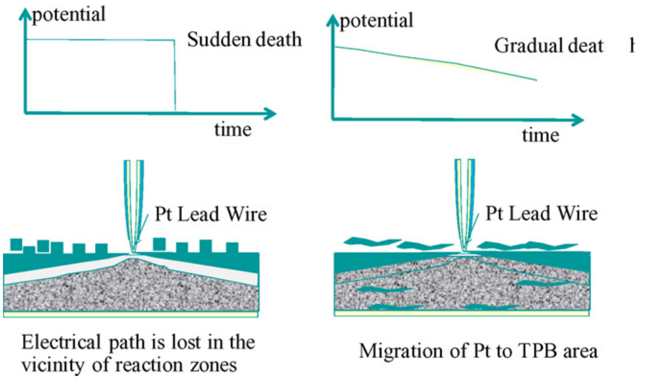

Fig. 1. Schematic comparison in electrical performance degradation between As and P in PNNL/NETL/WVU results [10,13–19].

2.1. *Comparison between As and P*

Both elements As and P show strong chemical affinity with nickel so that many intermetallic compounds are formed where nickel cermet anodes are encountered with such impurities. This is schematically illustrated in Fig. 1. Most interesting difference between two elements in degradation behavior is that As gives rise to a sudden death after no change in performance, whereas the performance degradation for the P case is observed from the beginning stage of contamination.

Fig. 2 collects the chemical potential diagrams in three different types. The first type is the Ellingham diagram for the M–O–H (M = As, P) systems. Gases in the H–O subsystem, namely, H_2(g), O_2(g), and H_2O(g), are assumed at a pressure of 1 atm, whereas gaseous species containing M (As or P) are assumed at $p = 10^{-6}$ atm; this corresponds to 1 ppm contamination in fuels. The second type of diagram is the extended Ellingham diagram for the Ni–M–O–H (M = AS, P) systems which indicates the dominant chemical form of nickel in the presence of M or M compounds. When only Ni or NiO are given, this indicates that Ni is stable against such contaminants. The third type of diagram is the $\log a(\mathrm{M})$ vs. $\log p(\mathrm{O_2})$ plot at a selected temperature (1073 K). From the chemical potential diagrams, the followings can be derived (Fig. 2):

(1) Both elements exhibit strong tendency of forming nickel intermetallic compounds such as Ni_5As_2 or Ni_5P_2. This is one of common features.
(2) For gaseous species, there are big differences between two elements. Although the thermodynamic data for such gaseous species are not necessarily accumulated well, the following difference is important: In an anode atmosphere, As exists as As_4 or As_2 molecules rather than AsH_3, whereas P exists as PH_3 or HPO_2 when water vapor exist.
(3) The formation of oxysalts ($Ni_3(AsO_4)_2$ or $Ni_3(PO_4)_2$) is favored in the oxidative atmospheres.
(4) When interactions with nickel are considered, the above differences give rise to significant differences between two elements:
    (i) At 1 ppm contamination level, only the intermetallic compound formation is a dominant process for the As contamination, whereas the intermetallic formation, the oxysalt formation or the no interaction due to the HPO_2 formation are competitive depending on temperature and oxygen potential.
    (ii) With decreasing concentration, the HPO_2 formation becomes favored. Note however, the oxysalt formation remains as possible process.