Doped La0.5Sr0.5MnO3 as Oxide Anode for Solid Oxide Fuel Cells using Dry C3H8 for Fuel

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論 文 名　：Doped $La_{0.5}Sr_{0.5}MnO_3$ as Oxide Anode for Solid Oxide Fuel Cells using Dry C_3H_8 for Fuel
(燃料に乾燥 C_3H_8 を用いる固体酸化物燃料電池のための $La_{0.5}Sr_{0.5}MnO_3$ 系酸化物アノード)

区　　分　：甲

論文内容の要旨

Direct hydrocarbon type solid oxide fuel cells are attractive from simple gas feed process and also high energy conversion efficiency. In this study, $La_{0.5}Sr_{0.5}MnO_3$ (LSM55) perovskite oxide was studied as oxide anode for direct hydrocarbon type SOFC. Although reasonable power density like 1 W/cm^2 and open circuit potential (1.1 V) at 1273 K was exhibited when H_2 was used as fuel, the power density as well as open circuit potential of the cell using LSM55 for anode was significantly decreased when dry C_3H_8 was used for fuel. After power generation measurement, LSM55 phase was decomposed to MnO and La_2MnO_4. Effects of various dopants to Mn site in LSM55 was studied and it was found that partial substitution of Mn in LSM55 with other cations, especially transition metal, is effective for increasing maximum power density. In particular, reasonable high power density can be achieved on the cell using Ni doped LSM55 for anode. On the other hand, Al substitution on the Mn site of LSM55 (LSMA) is effective for increasing stability against reduction and so, dopant effects of Al were studied in more details for dry C_3H_8 fuel. The improved phase stability is largely due to the stable feature of trivalent Al under reducing environment. The power density as well as open circuit potential increased with increasing Al content and the highest power density was achieved at $x = 0.4$ in $La_{0.5}Sr_{0.5}Mn_{1-x}Al_xO_3$ when using C_3H_8 fuel. Among the examined composition, it was found that the cell using $La_{0.5}Sr_{0.5}Mn_{0.6}Al_{0.4}O_3$ anode shows the largest power density (0.2 W/cm^2) at 1173 K and high open circuit potential (1.01 V) against dry C_3H_8 fuel. However, in order to further enhance the cell performance, effects of Co and Al co-doping to $La_{0.5}Sr_{0.5}MnO_3$ (LSMAC) for anode were studied. It was found that doping Co is effective for decreasing anodic IR loss and the power density could be much increased by doping Co for Mn site of Al-doped LSM. XRD measurement suggests that Co substituted Mn site over wide composition range and up to 40 mol%, partial substitution of Co in $LaMnO_3$ structure was successfully performed. The maximum power density was increased by doping Co for LSM doped with 10 mol% Al for both H_2 and C_3H_8 fuel. In particular, the smallest IR loss and anodic overpotential were achieved when 20 mol% Co was co-doped. The maximum power density of the cell using $La_{0.5}Sr_{0.5}Mn_{0.7}Al_{0.1}Co_{0.2}O_3$ (LSMAC72) was achieved at 953 and 246 mW/cm^2 for H_2 and C_3H_8

fuel at 1273 and 1173 K, respectively. Increase in power density can be assigned to the increased surface activity to the electrochemical oxidation by doping Co. Moreover, the oxide anode is shown to be tolerant to coking with no obvious formation of carbon structure, as proven by EDS, Raman spectra and XPS analysis suggesting its suitability as an anode for direct hydrocarbon fuel. Additionally, effect of composite LSMAC72 with oxide anodes was conducted to investigate the possibility of higher power density especially when using C_3H_8 fuel. $Sr_{0.94}Ti_{0.9}Nb_{0.1}O_3$ (STN), $Ce_{0.8}Gd_{0.2}O_2$ (GDC), $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ (LSGM), $La_{0.6}Sr_{0.4}Fe_{0.9}Mn_{0.1}O_3$ (LSFM) and $Ce_{0.6}Mn_{0.3}Fe_{0.1}O_2$ (CMF) were chosen as the constituent for composite with LSMAC72 owing to improved catalytic activity, phase stability or high electrical conductivity. Moreover, rather than initially reduced under H_2 fuel, the anode is directly supplied with dry C_3H_8 fuel. This changes in fuel setup greatly improved the cell performance and by directly feeding C_3H_8 without prior reduction in H_2, the cell performance of LSMAC72 at 1173 K doubled to ca. 530 mW/cm^2 from ca. 250 mW/cm^2 due to lower degree of phase decomposition. By adding oxide anode, the cell performance greatly increased and it was found that adding STN or CMF shows the most positive effects with MPD of more than 800 mW/cm^2 at 1173 K. Impedance arc and internal resistance analysis suggests that anodic overpotential is decreased when adding oxide anodes. However, the MPD rapidly dropped for LSMAC72+STN and most composites but LSMAC72+GDC shows fairly stable cell performance from 1173 K to 973 K. SEM micrograph reveals that there is barely any obvious change to the anode surface of LSMAC72+GDC and LSMAC72+LSGM but other composites particularly LSMAC72+LSFM shows microstructural changes after the power generation measurement in C_3H_8 at 973 K. Particularly, numerous porosity and interconnect of the particles are visible, allowing for better gas diffusion which leads to lower overpotential for LSMAC72+GDC. In addition, GDC enhanced the catalytic oxidation of C_3H_8, facilitating the kinetic of the fuel oxidation. In addition, GDC enhanced the catalytic oxidation of C_3H_8, facilitating the kinetic of the fuel oxidation. Increasing the GDC content shows positive effect to the MPD up to 20 wt% GDC. However, unexpectedly carbon formation is easier to deposit with GDC content higher than 30 wt% due to microstructural changes associated with higher GDC content. Nevertheless, this study has confirmed that enhanced power density can be achieved when LSMAC72 is mixed as a composite with GDC. Although stability of LSM perovskite structure is still insufficient in dry C_3H_8 atmosphere, doping Al is effective for increasing stability and so co-doping Al and Co to Mn site of $LaMnO_3$ is effective for decreasing anodic overpotential, hence Al and Co doped LSM55 particularly LSMAC72 shows great promise as an alternative anode for direct C_3H_8 type SOFC.