Electrode Reaction Kinetics at La$_{1-x}$A$_x$MnO$_3$($\gamma$) (A=Sr, Ca) / YSZ Interface

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Lanthanum manganite, an air electrode material of solid oxide fuel cells, is well known for its complicated nonstoichiometry, which depends upon oxygen partial pressure. This nonstoichiometry has a relationship with electrode reactivity as it affects oxygen activation step and/or oxide ion sink, etc (1,2). In addition, the cell volume of lanthanum manganite has a dependence on the nonstoichiometry. We report the relation between the cell volume (3) and the cathode reactivity, and the electrode reaction kinetics based on measurements of the crystal structure with X-ray diffraction and the steady-state polarization and the complex-impedance of the electrode system, O$_2$(g)/La$_{1-x}$A$_x$MnO$_3$($\gamma$)/YSZ, with P$_{O2}$ in the range of 10$^{-10}$ Pa and temperature at 873-1273 K.

The cathode material, La$_{0.6}$Sr$_{0.4}$MnO$_{3.95}$, was synthesized by the Pechini method and used for different cells LSM-1A and B. Powder X-ray analysis showed a single phase of the perovskite type. The complex-impedance under a polarized state was measured for LSM-1B. For the electrolyte, sintered YSZ (8 mole percent Y$_2$O$_3$) pellet was used. The electrochemical measurement was done with a three-terminal method. The complex impedance and steady-state polarization were measured using a frequency analyzer, a potentiostat, and a personal computer in O$_2$/Ar atmospheres of P$_{O2}$ = 10$^{-10}$ Pa at temperatures of 873-1273 K. Electrical measurements for La$_{0.55}$Sr$_{0.45}$MnO$_{3.9}$ (4) and La$_{0.9}$Ca$_{0.1}$MnO$_{3.9}$ (5) were carried out by same method and were reported elsewhere. The crystal structure was measured for La$_{0.6}$Sr$_{0.4}$MnO$_{3.95}$ and was reported elsewhere (3).

Up to now, the rate determining process for the electrode reaction at the porous La$_{1-x}$A$_x$MnO$_3$($\gamma$)/YSZ electrode has not been definitely clarified yet. However the current-potential relations (6) by many electrode measurements at the porous La$_{1-x}$A$_x$MnO$_3$($\gamma$)/YSZ electrode obey the Butler-Volmer equation for electrochemical reactions, Eq. 1, and the chemical processes, Eq. 2, (6),

\[ i = k(P_{O2})^{1/2} \exp(2F\eta_e/RT) - \exp(-2F\eta_e/RT) \]

\[ i = k (a_{O2}^{1/2} - P_{O2}(a_{O2}^{1/2})^n) \]  

Here, k is the rate constant, F (C/mol) is Faraday constant, \( \eta_e \) (V) is electrode over-potential, \( R/JK \) is gas constant, \( T/K \) is temperature, and \( a_{O2} \) is the oxygen activity in YSZ at the electrode/electrolyte interface. Eq. 1 and Eq. 2 can become the same equation as reported before (6).

The \( \sigma_e \) is defined at the equilibrium state of the electrode with gas phase as \( \sigma_e = (d\delta_e dE_{electrolyte})/dE_{electrolyte} \). From Eq. 1 and 2, we obtain:

\[ \sigma_e = (AF/RT)P_{O2}^{1/2} \]  

By fitting the experimental data of the steady-state polarization curves into Eq. 1 and the complex-impedance into Eq. 3, we obtain the rate constants, k. The k depends on the unit cell volume, \( V_{cell} \) of La$_{1-x}$Sr$_x$MnO$_3$. However, because we don't have the data of \( V_{cell} \) for La$_{1-x}$Ca$_x$MnO$_3$, we did not discuss LCM-4 further. \( k \) data obtained without gas diffusion depends on \( V_{cell} \) as shown for LMS-1B in Fig. 1. When \( V_{cell} \) increases, \( k \) increases in a proportionality relation. However, for low temperatures, the data has a scattering tendency and hysteresis, because the relaxation of oxygen nonstoichiometry in crystal lattice needs a long time and it depends on not only oxygen partial pressure but also electrode potential. As another cause, for low temperature, the increase of the surface coverage of adsorbed, O$_2$, influences the k of the O$_2$(g)/YSZ type cathode (7). Therefore we did not use the data of low temperature for fitting in Fig. 1.

![Figure 1. Unit Cell Volume dependence of log k for La$_{1-x}$Sr$_x$MnO$_3$-A (LSM-1A)/YSZ at 873 – 1273 K.](image)

From the relation of \( V_{cell} \) vs. log k, we observed that the tangent of \( V_{cell} \) vs. log k has a same value for same composition and the intercept may be different for different cells. We think that the intercept is a constant depending on amount of electrode reactivity sites, and length of three-phase boundary. Therefore using the average value of the slope for same electrode composition, we obtained a general equation for each electrode composition as shown in Table 1.

| Table 1. The reaction rate equation for La$_{1-x}$Sr$_x$MnO$_3$/YSZ. |
|-----------------|---------------------|
| \( k \) = \exp((1.892xV_{cell}/C)(P_{O2}^{1/2}/(exp(2F\eta_e/RT)-exp(-2F\eta_e/RT))) \) |
| \( k \) = \exp((1.505xV_{cell}/C)(P_{O2}^{1/2}/(exp(2F\eta_e/RT)-exp(-2F\eta_e/RT))) \) |