Electrode Reaction Kinetics at La$_{1-x}$A$_x$MnO$_{3+\delta}$ (A=Sr, Ca) / YSZ Interface

Kenji Yasumoto,[a] Junichiro Mizusaki,[b] Hibiki Itoh,[a]
Shaorong Wang,[c] Hiroaki Tagawa,[d] and Masayuki Dokiya[d]

[a] Smart Materials Science Department, Central Research Institute of Electric Power Industry, 2-6-1 Nagasaka, Yokosuka, Kanagawa 240-0196, Japan
[b] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
[c] Department of Applied Physics, College of Humanities and Sciences, Nihon University, 3-25-40 Sakurajousui, Setagaya-ku, Tokyo 156-8550, Japan
[d] Graduate School of Environment and Information Sciences, Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

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)/porous La$_{1-x}$A$_x$MnO$_{3+\delta}$/YSZ, with P_{O2} in the range of 10-10^5 Pa and temperature at 873-1273 K.

The cathode material, La$_{0.9}$Sr$_{0.1}$MnO$_{3+\delta}$, 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. 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} = 10-10^5 Pa at temperatures of 873-1273 K. Electrochemical measurements for La$_{0.8}$Sr$_{0.2}$MnO$_{3+\delta}$ (4) and La$_{0.6}$Ca$_{0.4}$MnO$_{3+\delta}$ (5) were carried out by same method and were reported elsewhere. The crystal structure was measured for La$_{1-x}$Sr$_x$MnO$_{3+\delta}$ 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$_{3+\delta}$/YSZ electrode has not been definitely clarified yet. However the current-potential relationships by many electrode measurements at the porous La$_{1-x}$A$_x$MnO$_{3+\delta}$/YSZ electrode obey the Butler-Volmer equation for electrochemical processes, Eq. 1, and the chemical processes, Eq. 2, (6),

$$i = k(P_{O2})^{1/2} [\exp(2F\eta_E/RT) - \exp(-2F\eta_E/RT)] \quad (1)$$
$$i = k (a_o^{el} - P_{O2}(a_o^{el})^{-1}). \quad (2)$$

Here, k is the rate constant, F (C/mol) is Faraday constant, η_E (V) is electrode over-potential, R (J/K mol) is gas constant, T (K) is temperature, and a_o^{el} 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 σ_E is defined at the equilibrium state of the electrode with gas phase as $\sigma_E = (di/dE_{el})_{Eel=(Eel)eq}$. From Eq. 1 and 2, we obtain:

$$\sigma_E = (4Fk/RT)(P_{O2})^{1/2}. \quad (3)$$

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_{unit}, of La$_{1-x}$Sr$_x$MnO$_{3+\delta}$. However, because we don't have the data of V_{unit} for La$_{1-x}$Ca$_x$MnO$_{3+\delta}$, we did not discuss LCM-4 further. log k data obtained without gas diffusion depends on V_{unit} as shown for LSM-1B in Fig. 1. When V_{unit} increases, log 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$_{ad}$, (θ) influences the k of the O$_2$(g)/Pt/YSZ type cathode (7). Therefore we did not use the data of low temperature for fitting in Fig. 1.

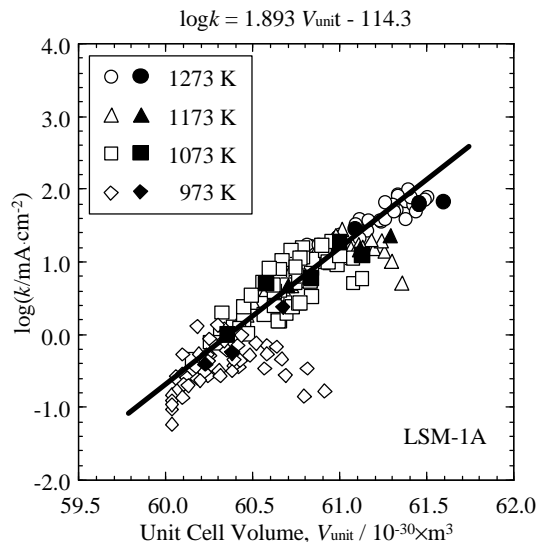Figure 1. Unit Cell Volume dependence of log k for La$_{0.9}$Sr$_{0.1}$MnO$_{3\pm\delta}$-A (LSM-1A)/YSZ at 873 – 1273 K.

From the relation of V_{unit} vs. log k, we observed that the tangent of V_{unit} 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 slop 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$_{3\pm\delta}$/YSZ.

LSM-1
$i = \exp\{1.892 \times V_{unit} - C\}(P_{O2}^0)^{1/2}[\exp(2F\eta_E/RT) - \exp(-2F\eta_E/RT)]$
LSM-2
$i = \exp\{1.505 \times V_{unit} - C\}(P_{O2}^0)^{1/2}[\exp(2F\eta_E/RT) - \exp(-2F\eta_E/RT)]$

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