A NEW CANDIDATE FOR THE SOFC CATHODE, Y_{0.9}Ca_{0.1}FeO_3: ELECTRICAL TRANSPORT PROPERTIES AND DEFECT STRUCTURE

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ABSTRACT

The total electrical conductivity, ionic conductivity and thermopower have been determined as functions of temperature (900 ≤ T/°C ≤ 1100) and oxygen partial pressure (10^{-16} ≤ P_{O_2}/atm ≤ 1) on the system of Y_{1-x}Ca_xFeO_3 (x=0.1), a newly proposed SOFC cathode material. The majority ionic carriers have been found to be oxygen ions via electrotransport experiments. The ionic conductivity, which is in the range of 10^{-3} to 10^{-1} S/cm at e.g. 1100°C, tends to increase with increasing P_{O_2} in oxidizing atmospheres and with decreasing P_{O_2} in reducing atmospheres. The defect structure on the basis of anti-Frenkel disorder and the phase stability are discussed.

INTRODUCTION

Men's endeavor to search for better materials will never end until absolutely the best material has finally been found for a specific application. Obviously, the cathode materials for solid oxide fuel cell applications are not the exception. As an attempt to excavate a better candidate for the cathode material, we have been examining transport properties of the system of YFeO_3(1). It has been found that the p-type conductivity can be enhanced much enough for the cathode applications by incorporating CaO up to ca. 10 m/o, which seems to be the solubility limit, and that the majority carrier holes migrate via a small polaron mechanism with a hopping energy of 0.15–0.19 eV. The defect structure of the system has been proposed on the basis of the Schottky disorder (0=V_{Y}^++V_{Fe}^{3+}+3V_{O}^{2-}) and the disproportionation of Fe^{3+} (2Fe^{3+}=Fe^{2+}+Fe^{4+}). Nevertheless, the ionic
conductivity, which is another important property of a cathode material, has not yet been characterized and the major ionic defect(s) remains unidentified.

This paper is concerned with the ionic conductivity, the electronic conductivity, the thermoelectric power, and the identity of the major ionic defect for the system of 10m/o CaO-doped YFeO3 or Y0.9Ca0.1FeO3. On the basis of the isothermal variations of these properties against oxygen partial pressure, the defect structure of the oxide will be established more clearly and the stability limit estimated.

**EXPERIMENTAL PROCEDURE**

Y0.9Ca0.1FeO3 samples were prepared by conventional ceramic processing(1): The 99.9% pure powders of Y2O3 (Rare Metallic, Japan), Fe2O3 (Aldrich, USA), CaCO3 (Shimakyu's Pure Chemical, Japan) were mixed in the appropriate ratio and calcined at 900°C for 10 hours in air. The calcined samples were ground, cold-pressed isostatically at 58.8 MPa, and finally sintered at 1350°C for 15 hours in the air atmosphere.

The total electrical conductivity was determined by the conventional d.c. 4-probe technique and the thermopower by a heat pulse technique(1,2) both simultaneously on parallelepiped specimens measuring ca. 1.5mm x 1.5mm x 10mm. The ionic conductivity was determined from electron blocking cells, Po2, Pt/ZrO2(+8m/oY2O3)/Y0.9Ca0.1FeO3/ZrO2(+8m/oY2O3)/Pt, Po2, by an a.c. impedance spectroscopy combined with the Fourier–Laplace transform of dc relaxation which is a time–domain representation of lower frequency impedances. Combination of these two partial impedance spectra, i.e. one instrumentally obtained and the other transformed, yields a complete spectrum over the practically full frequency range of 0 to ∞ Hz. The ionic conductivity can then be extracted from the Warburg impedance at the lowest frequency part. The readers are referred to Ref. 3 or 4 for the details of this novel technique, which has been recently established to directly determine the ionic conductivity of an electronic conductor.

The majority ionic charge carrier of the oxide was identified by electrotransport experiments, in which the material transport or the crystal
shift was monitored while passing a current via the oxygen gas electrodes as in Morin's experiments (5) to determine the ionic transference number of CoO. If cations are mobile, the oxide is destroyed at the anode and the transported cations create lattice molecules of the oxide at the cathode, which thus causes a drastic microscopic change in the vicinity of both electrodes. If the oxide anions are practically exclusively mobile, on the other hand, no change takes place at all. Experimental details are referred to Refs. 4 and 7.

RESULTS AND DISCUSSION

The electrical conductivity (\(\sigma\)) and thermoelectric power (\(\theta\)) vary against oxygen partial pressure (\(P_{O_2}\)) at various temperatures as illustrated in Figs. 1(a) and (b), respectively. One may recognize that each of the isotherms of conductivity or thermopower can be divided into two regions, one \(P_{O_2}\)-independent at higher \(P_{O_2}\) values and the other \(P_{O_2}\)-dependent at lower \(P_{O_2}\) values. The presence of a thermopower maximum in the latter \(P_{O_2}\)-dependent region tells that even this region may be divided further into two: the p-type carrier dominated region to the right of the maximum and the electron–hole mixed region to the left.

By combining two partial impedance spectra, one directly measured with a commercial impedance analyzer, HP4192A and the other Fourier–Laplace transformed from d.c. relaxation results, complete impedance spectra have been constructed in an essentially entire range of frequency as demonstrated in Fig. 2. The ionic conductivity of the electronic conductor specimen has been subsequently determined from the lowest frequency Warburg impedance via a nonlinear fitting to the appropriate equivalent circuit as detailed earlier (4). The result, the ionic conductivity of \(\text{Y}_{0.9}\text{Ca}_{0.1}\text{FeO}_3\) at 1100°C is shown against oxygen partial pressure in Fig. 3 where the 4-probe (total) conductivity is shown together for comparison. The ionic conductivity is in the range of \(10^{-3}\) to \(10^{-1}\) S/cm depending on oxygen partial pressures at, e.g. 1100°C. Upon comparison with the total conductivity, the ionic transference number varies in the range of \(t_{\text{ion}}=10^{-4}\) to \(10^{-2}\). It is noted that, as \(P_{O_2}\) decreases from \(P_{O_2}=1\) atm, the ionic conductivity first decreases with a slope of approximately 1/2, then remains flat, and finally increases with a lesser slope.
In the electrotransport experiments in which a current of 1A was passed at 1160°C in the air atmosphere for 24 hours, no change has been found in the vicinity of both electrodes. This result unambiguously indicates that the major ionic carrier of our system is oxide ions.

Defect Structure

Since the ionic transference number is no greater than 0.13 over the entire range of oxygen partial pressure examined, e.g., at 1100°C as demonstrated in Fig. 3, the 4-probe conductivity may be regarded as essentially electronic. Furthermore, the corresponding thermopower isotherm in Fig. 1(b) indicates that the majority electronic carrier is holes down to log (Po2/atm) = −8.2, where the thermopower maximum falls, and therefrom electronic contribution begins to be appreciable.

When a conductivity minimum (σ_{min}) is located on a conductivity isotherm, one can distinguish, with relatively better precision, the oxygen exponent(s) of the conductivity. The total (electronic) conductivity in Fig. 1(a) can be given as

\[ \sigma = \sigma_{\text{min}} \cosh (\frac{1}{2} \ln \alpha) ; \quad \alpha = \sigma_p/\sigma_n = p/nb. \tag{1} \]

where \( \sigma_p \) and \( p \) are respectively the partial conductivity and concentration of holes, \( \sigma_n \) and \( n \) are the corresponding quantities for electrons, and \( b(=\mu_n/\mu_p) \) the mobility ratio of electrons(\( \mu_n \)) to holes(\( \mu_p \)). Since \( \sigma_p \propto P^{-m}o_2 \) and \( \sigma_n \propto n^{-1/m} P^{-1/m}o_2 \) in general,

\[ (\sigma \log \alpha / \sigma \log P_2) = 2/m \tag{2} \]

assuming \( b \) is independent of \( P_2 \). One can thus evaluate the reciprocal oxygen exponent \( m \) from a plot of \( \log \alpha \) vs. \( \log P_2 \) with a better precision than the conventional treatment. The result is shown in Fig. 4, where one can unambiguously distinguish three \( P_2 \) regions, e.g., at 1100 °C, i) \( P_2 \leq \text{ca. } 10^{-8} \text{ atm where } m=6 \text{ (the best estimate via a linear regression is } m=6.3 \pm 0.1) \); ii) \( 10^{-8} < P_2/\text{atm} < \text{ca. } 10^{-3} \text{ where } m=4 \text{ (the best estimate, } m=4.3 \pm 0.1) \); iii) \( 10^{-3} < P_2/\text{atm} \text{ where } m=\infty \). As temperature decreases, the region boundaries tend to shift leftward, but the oxygen exponent in each region remains the same within experimental error.
The result from the electrotransport experiments and the ionic conductivity in Fig. 3 indicates that the type of the majority ionic defect is anti-Frenkel disorder, \((O^\prime\prime, V_o^-)\). The presence of interstitial oxide ions as majority ionic defect has not ever been thought of for similar systems, but an increase of the anionic conductivity with \(P_{O_2}\) in the region of \(m=\infty\) in Fig. 3 renders this conclusion unavoidable.

On the basis of these pieces of electronic and ionic information, one can immediately envisage the defect structure of the system as

\[
\text{nil} = e + h ; \quad K_i = np \tag{3}
\]

\[
O_o^\prime\prime = O_l^\prime\prime + V_o^- \quad ; \quad K_F = [O_l^\prime\prime][V_o^-] \tag{4}
\]

\[
\frac{1}{2}O_2(g) = O_l^\prime\prime + 2h \quad ; \quad K_{ox} = [O_l^\prime\prime]P_{O_2}^{-1/4} \tag{5}
\]

with the charge neutrality condition

\[
n + 2[O_l^\prime\prime] + [CaY\prime] = p + 2[V_o^-] , \tag{6}
\]

where \(K_{t}(t=i,F,ox)\) denotes the equilibrium constant for the corresponding defect formation reaction. The sequence of majority defect pairs can then be identified with increasing \(P_{O_2}\) in its range examined as

i) \((e^-, V_o^-)\) where \(m=6\) or \(p \propto P_{O_2}^{1/6}\),

ii) \((V_o^\prime\prime, CaY\prime)\) where \(m=4\) or \(p \propto P_{O_2}^{1/4}\);

iii) \((CaY\prime, h^-)\) where \(m=\infty\) or \(p \propto P_{O_2}^0\).

Isothermal variation of each defect concentration as solved from eqs. [3]-[6] is illustrated in Fig. 5. This defect structure very reasonably explains the measured ionic and electronic conductivities as depicted by the solid lines in Fig. 3. It is suggested that the oxygen interstitial has a mobility much higher than the oxygen vacancy and for electronic carriers \(\mu_p > \mu_o\).

**Phase Stability**

Once \(P_{O_2}\) was lowered below the leftmost datum on each isotherm of
Fig. 1, the voltage drop or thermopower signal normally became so fluctuating that the equilibrium properties could not be determined. This fact suggests that the phase stability limit has been exceeded(8). It is supported by the observation that a specimen which had once been left below this limiting Po2 failed to reproduce the previous properties upon reoxidizing.

The expected stability limit as read from these isotherms is shown in Fig. 6. The decomposition enthalpy is estimated from the slope as 90±20 kcal/mol-O2, which is comparable to the decomposition enthalpies found for the similar systems, e.g., 107 kcal/mol-O2 for LaFeO3(9).

CONCLUSION

From the above, we can conclude: The majority ionic carrier of the system Y0.9Ca0.1FeO3 is oxide ions and the ionic transference number takes a value in a range of 10^-4 to 10^-2 depending on oxygen partial pressure at 1100°C. The type of ionic defect is anti-Frenkel defect and the oxygen interstitial has a much higher mobility. The majority defect type varies sequentially from (h', Cay') to (Cay', Vo') to (Vo', e') as Po2 decreases from 1 atm. The system becomes thermodynamically unstable below Po2=10^-15, 10^-13, 10^-13 atm at 900 °C, 1000 °C and 1100 °C, respectively.

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REFERENCES

1. H.-I. Yoo and C.-S. Kim, Solid State Ionics, 53-56, 583 (1991).
2. H.-I. Yoo and J.-H. Whang, J. Phys. Chem. Solids., 53, 973 (1992).
3. J.-S. Lee, Ph. D Thesis, Seoul National University, (1994).
4. J.-S. Lee and H.-I. Yoo, Solid State Ionics, 68, 139 (1994).
5. F. Morin, J. Electrochem. Soc., 126, 760 (1979).
6. Y.-I. Jang, M.S. Thesis, Seoul National University, (1995).
7. H. Becker and H. P. R. Frederiks, J. Appl. Phys. Suppl., 33, 447 (1962).
8. J. Mizusaki, T. Sasamoto, W. R. Cannon and H. K. Bowen, J. Am. Ceram. Soc., 66, 247 (1983).
9. T. Nakamura, G. Petzow and L. J. Gauckler. Mat. Res. Bull., 14, 649 (1979).
Fig. 1. Variation of the total conductivity (a) and thermopower (b) against oxygen partial pressure ($P_{O_2}$) for the system of $Y_{0.9}Ca_{0.1}FeO_3$ at 900°C, 1000°C and 1100°C, respectively. Note that each isotherm may be divided into a $P_{O_2}$-independent region and a $P_{O_2}$-dependent one.

Fig. 2. Construction of complete impedance spectra over the practically full frequency range (0 to $\infty$ Hz) for an electron-blocking cell, $P_{O_2}$, Pt/YSZ/$Y_{0.9}Ca_{0.1}FeO_3$/YSZ/Pt, $P_{O_2}$, by combining instrumentally measured spectra (○) with the Fourier-Laplace transforms of dc relaxation results (●). The ionic conductivity ($\sigma_{ion}$) can be extracted from the lowest frequency Warburg impedances. The solid lines are the best fitted.
Fig. 3. The ionic conductivity ($\bullet$) of $Y_{0.9}Ca_{0.1}FeO_3$ at 1100°C, as determined from the full spectra in Fig. 2. The total conductivity ($\blacksquare$) isotherm (1100°C) is also shown for comparison. The solid lines represent the partial conductivities by free electrons ($\sigma_e$), by holes ($\sigma_h$) and by the oxide anions ($\sigma_{ox}$), expected from the defect structure proposed in Fig. 5.

Fig. 4. Log $a$ (= $\sigma_e/\sigma_{ox}$) against log $P_{O_2}$ as derived from the conductivity isotherms in Fig. 1(a). Three $P_{O_2}$-regions where $m=6$, 4, and $\infty$, respectively, $m$ being the reciprocal oxygen exponent of the conductivity, are readily distinguished on each curve.
Fig. 5. Defect structure of Y_{1-x}Ca_xFeO_3 based on the electrical property isotherms of Figs. 1 and 3.

Fig. 6. Stability limits of (Y_{0.9}Ca_{0.1})FeO_3 at 900°C, 1000°C and 1100°C. The orthoferrite phase is thermodynamically stable above the dotted line.

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