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Ionic Conductivity of Potassium Samarium Silicates and Its Application as an Electrochemical CO₂ Gas Sensor

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1 INTRODUCTION

Recently, there has been considerable interest in dense ionic conductors because a dense ionic conductor is a preferable material for solid state batteries and/or chemical sensors¹⁻⁹. As part of a screening program for well compacted and conductive alkali ion solid electrolytes, the electrical properties of some lanthanoid - silicates have been studied in which the anion is a three dimensional network of interconnected LnO₆ octahedra and SiO₄ tetrahedra. For M₂O-Ln₂O₃-2SiO₂ (M=Li, Na, K, Rb, Cs; Ln = La, Nd, Sm, Gd, Dy, Y, Er, Yb), the highest ionic conductivity was observed for K₂O-Nd/Sm₂O₃-2SiO₂ with a hexagonal phase⁹. The materials acts as a good potassium ionic conductor. Here we present the electrical properties of K₂O-Sm₂O₃-nSiO₂ and CO₂ gas sensing characteristics of an electrochemical solid state cell with O₂/Pt || K₂O-Sm₂O₃-nSiO₂ | Na₂CO₃ || Pt, O₂, CO₂ structure.

2 EXPERIMENTAL

As starting materials, reagent grade K₂CO₃, Sm₂O₃ and SiO₂ were used. The raw materials were ball-milled with ethanol, dried, and calcined in air. The obtained powders were ball-milled again with ethanol into fine powders, to which an amount of 15 % of polyvinylalcohol solution was added. After drying, discs were pressed at 1000 kg/cm² and sintered in air. The discs were 8 mm in diameter and ca. 2 mm thickness. Some discs were ball-milled again and then immersed in water. The treated powders were pressed again and then sintered (water treated ceramics). Platinum paint was applied to both faces of the disc and heated to 950 °C.

The electrical properties were measured using a multi-frequency LCR meter in the frequency range of 100 Hz ~

10 MHz (Yokogawa Hewlett-Packard, 4292A). The sample was heated up to 300 °C to eliminate the adsorbed water before measurements were made. The crystalline phases were identified at room temperature by x-ray diffraction technique. The microstructures were examined using scanning electron microscopy (SEM).

3 RESULTS AND DISCUSSION

For K₂O-Sm₂O₃-nSiO₂, dense ceramics were obtained, except for n=1 as shown in Fig.1. For the samples with higher contents of SiO₂ (n>4), well defined fine particles were not observed and the densification well progressed. Crystal parameters with sintering temperature are summarized in Table I and hardly influenced by SiO₂ content except for n=1.

To determine the conductivity component, complex-plane impedance analysis was performed. In the lower temperature region, the result was represented by a slightly depressed semicircle which passed through the origin, in a higher frequency region and by a spur in a lower frequency region. The intercept with the Z'-axis indicates the resistance of the electrolyte and the spur is attributable to the electrode-electrolyte junction. When the temperature increased, the semicircle diminished, and only a quasi-straight line due to the electrolyte-electrode behaviour was observed, in which the intercept with the Z'-axis indicates the total resistance of the electrolyte. A depressed semicircle appearing in the high frequency region in the complex impedance plot can be adequately expressed by Equation 1:

$$Z(\omega) = Z_0 / [1 + (j\omega/\omega_0)^{1-\alpha}] \quad [1]$$

where Z(ω) is the complex impedance at angular frequency ω, Z₀ the low frequency real-axis intercept, ω₀ the relaxation angular frequency at the maximum height of the semicircle, α the depression parameter and j = (-1)^{1/2}. The equivalent circuit corresponding to the impedance spectrum consists of a frequency dependent capacitor C_p(ω) and a frequency independent resistor R_p. These parameters are described by the following equations

$$Z_0 = R_p, \quad C_p(\omega) = C_0(j\omega/\omega_0)^{-\alpha}, \quad R_p C_0 \omega_0 = 1$$

The limiting case, α = 0, represents an equivalent circuit consisting of lumped RC components with zero depression

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A

B

C

Fig. 1 Scanning electron micrographs (bar=2 μ m).

A) $\text{K}_2\text{O-Sm}_2\text{O}_3\text{-2SiO}_2$, B) $\text{K}_2\text{O-Sm}_2\text{O}_3\text{-4SiO}_2$, C) $\text{K}_2\text{O-Sm}_2\text{O}_3\text{-6SiO}_2$

angle.

It is confirmed for the series of $\text{K}_2\text{O-Ln}_2\text{O}_3\text{-nSiO}_2$ that the depression angle decreases with an increase in the resistance (the resistance increases with SiO_2 content except for $n = 1$) and that the ω_0 -value increases with the temperature. Graphically estimated resistances from the complex plane impedance results were parameterized by the Arrhenius equation,

$$GT = G_0 \exp(-E/kT) \quad [2]$$

where G is the conductivity ($=1/R$), G_0 is the pre-exponential factor, E is the activation energy, k is Boltzmann's constant,

Table 1 Crystal parameters (Hexagonal) and sintering temperature.

Materials	a/nm	c/nm	sintering temp./ $^\circ\text{C}$
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-2SiO}_2$	0.9478	0.6992	350/10h
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-3SiO}_2$	0.9511	0.7012	1200/3h
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-4SiO}_2$	0.9512	0.7006	1050/3h
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-5SiO}_2$	0.9507	0.6991	950/3h
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-6SiO}_2$	0.9511	0.6998	950/3h
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-7SiO}_2$	0.9511	0.6996	950/3h
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-8SiO}_2$	0.9509	0.6998	950/3h
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-10SiO}_2$	0.9509	0.6990	950/3h
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-12SiO}_2$	0.9509	0.6983	1000/3h
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-14SiO}_2$	0.9505	0.6985	1000/3h

and T is the absolute temperature. Arrhenius plots are shown in Fig. 2. Electrical parameters are summarized in Table 2. The highest conductivity is observed for $\text{K}_2\text{O-Sm}_2\text{O}_3\text{-3SiO}_2$, and conductivity decreases with increasing SiO_2 content.

Fig. 2 Temperature dependence of conductivity. n in $\text{K}_2\text{O-Sm}_2\text{O}_3\text{-nSiO}_2$ is shown in this figure

For the cell, expressed as:

it is assumed that the chemical potential at the anode is controlled by the reaction:

whereas that at the cathode by the equation:

Table 2 Electrical parameters.

Materials	Conductivity/ Scm^{-1}		E/kJmol^{-1}
	500 °C	600 °C	
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-SiO}_2$	$<10^{-8}$	$<10^{-8}$	161
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-2SiO}_2$	1.71×10^{-2}	2.00×10^{-2}	32.8 (18.0)
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-3SiO}_2$	3.95×10^{-2}	5.07×10^{-2}	39.9 (20.9)
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-4SiO}_2$	3.52×10^{-4}	9.46×10^{-4}	50.6 (42.9)
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-6SiO}_2$	9.28×10^{-6}	3.61×10^{-5}	79.7
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-7SiO}_2$	8.20×10^{-6}	3.17×10^{-5}	86.1
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-8SiO}_2$	3.96×10^{-6}	1.64×10^{-5}	87.4
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-10SiO}_2$	2.80×10^{-6}	1.16×10^{-5}	89.5
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-12SiO}_2$	1.02×10^{-6}	4.90×10^{-6}	104.9
$\text{K}_2\text{O-Sm}_2\text{O}_3\text{-14SiO}_2$	6.57×10^{-7}	2.99×10^{-6}	94.9

The overall reaction is predicted to

When Po_2 in the cathode side is the same as that in the anode side, the e.m.f. of the cell is then expected to be

$$\text{emf} = -[\Delta G_{\text{K}_2\text{O}} + \Delta G_{\text{CO}_2} + 2\Delta G_{\text{Na}^+} - \Delta G_{\text{Na}_2\text{CO}_3} - 2\Delta G_{\text{K}^+}] / 2F$$

$$- (RT / 2F) \ln [a_{\text{K}_2\text{O}} a_{\text{Na}^+}^2 P_{\text{CO}_2} / a_{\text{K}^+}^2] \quad [6]$$

where ΔG is the standard free energy of formation and a_i the activity of species "i", and P_{CO_2} the partial pressure of CO_2 . If the activity of K_2O , K^+ and Na^+ remains constant, the emf gives the concentration of CO_2 .

Fig.3 CO_2 sensing characteristic of $\text{K}_2\text{O-Sm}_2\text{O}_3\text{-4SiO}_2$ based element under dry condition at 470 °C.

Fig.3 shows the sensing characteristic at 470 °C for the sensor with a structure;

On switching from 1000 ppm CO_2 /air flow to 100 ppm CO_2 /air flow, the emf increased quickly and a steady state value was observed within 2 min. The raise and recovery

Fig.4 CO_2 sensing characteristic of $\text{K}_2\text{O-Sm}_2\text{O}_3\text{-4SiO}_2$ based element under wet condition at 470 °C.

times were very fast; the 90% response time was less than 1 min (test gas flow rate = 40 ml/min and measuring chamber volume ~ 60 ml). When the CO_2 concentration changed from 10000 ppm to 100 ppm, from 100 ppm to 10 ppm and from 10 ppm to air, the response time becomes longer. It

Fig.5 Sensing characteristic of $\text{K}_2\text{O-Sm}_2\text{O}_3\text{-4SiO}_2$ based element when CO_2 concentration was repeatedly changed from 100 ppm to 1000 ppm and reversed in wet and then in dry.

seems that the concentration in the measuring cell could not be obtained in an early period after changing from a higher to a lower concentration since the response time becomes faster with an increasing flow rate. The response time shortened by an increase in the flow rate of the test gases and with an increase in the number of measuring cycles. With increasing SiO_2 content, the observed emf was increased because of the lowering of K_2O activity in the electrolyte.

The influence of moisture of the sensing characteristics should be considered. Figure 4 shows the result under wet conditions. When the humid test air (30 °C dew point) was passed, the emf value was lower than that for the dry test air. The emf in a lower concentration of CO_2 less than 100 ppm was lower than that the value expected from the relation confirmed in a higher range (> 100 ppm) and the decrement of the emf had a tendency to growing with a decrease in CO_2 concentration while the sensing characteristics recovered completely after the water vapour was cut off as shown in Fig.5. These decrements are interpretable by the formation of sodium oxides such as Na_2O and Na_2O_2 in Na_2CO_3 layer and/or Pt electrode-body interface as reported previously ⁷.

4 CONCLUSION

Dense ceramic-glass composites ($\text{K}_2\text{O}-\text{Sm}_2\text{O}_3-n\text{SiO}_2$, $n > 3$) is produced directly by the sintering of starting mixtures. The ionic conductivity lowered with an increase in SiO_2 content for the sample with hexagonal structure in which the lattice parameters were hardly influenced by the SiO_2 content. CO_2 sensing characteristics of electrochemical gas

sensor with a structure expressed as; $\text{O}_2, \text{Pt} \parallel \text{K}_2\text{O}-\text{Sm}_2\text{O}_3-n\text{SiO}_2 \mid \text{Na}_2\text{CO}_3 \parallel \text{Pt}, \text{O}_2, \text{CO}_2$ were investigated in terms of a two electron electrochemical reaction. The emf is sensitive to CO_2 gas concentration and increases with n in $\text{K}_2\text{O}-\text{Sm}_2\text{O}_3-n\text{SiO}_2$. The introduction of water vapour induced a prolonged response time and a lowering of the emf, in which the decrement increased with a decrease in CO_2 concentration and the sensing characteristics recovered completely after the water vapour was cut off.

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