Mixed Proton Electron Conductivity of Calcium Chromate(V) Apatite

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This is the first report to investigate on the electrical conductivity of unusual high valence state pentavalent chromium oxides in terms of defect thermodynamics. Calcium chromium(V) apatite was prepared as a single phase, and the electrical conductivity was examined as a function of oxygen partial pressure \( p_{O_2} \). The conductivity was increased at higher \( p_{O_2} \) in wet atmosphere but it was not dependent on \( p_{O_2} \) in dry atmosphere. The water concentration cell gives stable electromotive force. The features disclosed that the chromium(V) apatite reveals proton electron mixed conductivity under wet oxidative condition.

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The apatite is a group of rare earth or alkaline earth salts of tetrahedral \( MO_4 \) oxoanions (\( M = P^{5+}, Si^{4+}, Ge^{4+}, As^{3+} \text{ etc.} \)). Early studies have revealed that there are many interesting characteristics in these materials. The most important one, however, is their oxide ion conductivity. Apatite oxide ion conductors (rare earth silicates) were first found by Nakayama et al. in 1995.1,2 They show fairly high oxide ionic conductivity in an intermediate temperature range of 500–800 °C.3 In addition, they have high transport numbers which are very close to 1.0 with a wide oxygen partial pressure range,4 thus being considered as candidates for intermediate temperature solid oxide fuel cell (IT-SOFC) electrolytes.

Typical apatite-type oxides tend to be electronically insulating because of the nature of the constituent cations with closed-shell configuration. Meanwhile, apatite-type calcium chromate(V), \( Ca_3(CrO_4)_2(OH) \), comprising from \( CrO_4^{2-} \) oxoanions are reported to reveal semiconductor characteristics at elevated temperature because of the mobile electrons derived from d\(^{1}\) configuration Cr\(^{3+}\) ions.5 Hence, it is reasonably expected that this compound retains superimposed electronic conduction and ionic conductivity at intermediate temperatures. Such a material is promising for the cathode/anode materials of fuel cells, gas separation membranes and so on.6,7 In this study, we investigate on the electrical conduction behavior of apatite-type calcium chromate(V) under various oxygen partial pressure in order to explore the feasibility of mixed ion electron conductivity in apatite phase.

Experimental

Apatite-type calcium chromate was prepared by thermal decomposition of \( Ca^{4+}-Cr^{3+} \) mixed precursors.8,9 \( Ca(CH_3COO)_2 \) (99.9% purity, Kanto) and \( CrO_3 \) (99.9% purity, Kanto) powders were dissolved into a sulfuric acid solution by the disproportionation reaction of \( Cr^{3+} \) ions, and the doses was titrated by the same method to determine the total concentration of chromium, \( C_{Cr} \). Hence, the oxidation state of chromium, \( Z_{Cr} \), is given by the following

\[
Z_{Cr} = (6 \cdot C_{Cr} + 3(C_{Cr} - C_{VI})) / C_{tot} \tag{2}
\]

The valence state of chromium was also investigated by X-ray photoelectron spectroscopy (XPS) (JEOL JPS-9200). High-resolution XRD patterns were measured by a RIGAKU diffractometer under the following conditions: Cu Kα, 40 kV, 20 mA; scanning step, 0.03° (20); counting time, 20 s/step; 20 range, 10–110°. Rietveld structure refinement was carried out using the RIETAN program. Crystallographic data for calcium hydroxyl apatite10 was used as a starting model for all compounds. Fine Pt wires (0.05 mm) were attached to the pellets with Pt paste (Nilaco). The electromotive force (EMF) were measured with a concentration cell with the calcium chromate disks (12 mm diameter and 1 mm thickness) sandwiched by Pt electrode. The disk was prepared by CIP and Pt electrode was deposited by applying Pt paste with calcination at 800°C. Before, EMF measurements, the permeation tests were conducted in order to check the gas tightness of the disk. The mixed \( N_2 \) and \( Ar \) gas (50% \( N_2 \)) was fed to one side of the disk and pure \( Ar \) gas to the other side. The gas phases in the pure \( Ar \) side were examined by Gas Chromatograph (GL science GC3000). The water concentration cell was constructed at 800°C by exposing a flow of humidified air (\( Ar/O_2 = 4/1 \)) on one side of the cell and dried air on the other side. The dried gases (\( p_{H_2O} = 0.12 \text{ kPa} \)) were prepared by passing through CaCl\(_2\) drying agents and the humidified (\( p_{H_2O} = 3 \text{ kPa} \)) was prepared by bubbling in water at 25°C. The oxygen concentration cell was constructed by exposing a flow of dried pure \( O_2 \) gas on one side of the cell and dried air on the other side. The voltage at high concentration side was measured relative to low concentration side.

Results and Discussion

Apatite-type calcium chromate can be prepared as a single phase by the preparation procedures mentioned above. Hereafter, apatite-type calcium chromate is denoted as \( Ca-Ap \). EPMA measurements indicates that the atomic ratio of calcium, chromium and oxygen in \( Ca-Ap \) is given by \( Ca/Cr/O = 5.00/3.00/12.7 \). The oxidation state of chromium, \( Z_{Cr} \), was determined to be +5.05 ± 0.07 by chemical titration, indicating that nominal valence state is +5. The Cr 2p XPS spectra revealed the 2p\(_{1/2}\) and 2p\(_{3/2}\) peaks at 579.0 eV and 588.3 eV.
respectively. These features are in good agreement with those of pentavalent chromium compound NdCrO₅.² This is in agreement with the previous reports on the identification of the chromium valence state in apatite type calcium chromate by using Cr K-edge XANES spectroscopy.² These conclude that Cr-Ap has Cr ions only in Cr⁵⁺ valence state. The chemical composition of Cr-Ap can be given by Ca₅(CrO₄)₃(O, OH)₀.₇, where O²⁻ sites are partially occupied by both O₂⁻ and OH⁻ ions as is the case with typical hydroxy-apatite phases.¹⁰

Rietveld structural refinement was conducted with the sample sintered at 930 °C for 12h in wet Ar atmosphere (Fig. 1). The refinement converges well and G of F indicator is enough small, confirming that a single phase of the calcium chromium apatite (S. G. P6₃/m, hexagonal) is isolated. The refined structural parameters were listed in Table I. The lattice constants determined here are in agreement with the previously-reported.⁻³ The atomic Ca/Cr/O ratio is given by 5.00/3.00/12.₇, which is very close to one determined by EPMA. Therefore, Cr-Ap can be represented by Ca₅(CrO₄)₃(O, OH)₀.₇ when cationic charge is compensated by proton to fix the Cr valence at +5.

Figure 1. Rietveld structure refinement profile of powder X-ray diffraction of Cr-Ap. Space group: P6₃/m. Reliability factors: Rwp = 12.3%, Rp = 10.5%, Rg = 14.0%. Goodness of fit: Rwp/Rg = 1.62.

Figure 2. Electrical conductivity σ of Cr-Ap in (a) dry and (b) wet atmosphere as a function of oxygen partial pressure pO₂. Inset of (a) shows Arrhenius plot of σ at pO₂ of 0.1 atm in dry and wet atmosphere.

Table I. Lattice parameters of Cr-Ap, given by Rietveld refinements.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>Occupancy</th>
<th>a / nm</th>
<th>c / nm</th>
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</thead>
<tbody>
<tr>
<td>O1</td>
<td>6h</td>
<td>1.0</td>
<td>0.96670(4)</td>
<td>0.70341(5)</td>
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</tbody>
</table>

Atomic coordinates

<table>
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<tr>
<th>Atom</th>
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<th>Occupancy</th>
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<th>y</th>
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<tr>
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<tr>
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<td>0.1859</td>
<td>0.0385</td>
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</tr>
<tr>
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<tr>
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<td>-0.0055</td>
<td>0.14</td>
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</table>

Cr-Ap reveals semiconductor characteristics in the 800–920 °C range in both wet and dry atmospheres: The ln conductivity increases with increasing temperature (inset of Fig. 2a). Furthermore, the activation energy in dry atmosphere (0.13 eV) is smaller than that in wet atmosphere (0.27 eV). This reveals that the conduction mechanism is changed by humidity.

The electronic carrier concentrations can be variable through the equilibrium between oxygen deficits and oxygen gas.

\[ \frac{1}{2}O_2 + V_0^{**} \rightleftharpoons O_0^{*} + 2h^* \quad \{K_5 = [h^*]^2 [V_0^{**}]^{-1} pO_2^{0.5}\} \quad [3] \]

Here, oxygen defects \( V_0^{**} \), lattice oxygen \( O_0^{*} \) and electron hole \( h^* \). Figure 2a shows that conductivities of Cr-Ap were essentially independent on \( pO_2 \) in dry atmosphere, indicating that the charge carrier concentrations are not varied by \( pO_2 \). It is presumed that the reaction 3 is not progressive in Cr-Ap in dry atmosphere since the valence state of Cr atoms is not flexibly changed by releasing oxygen (Eq. 4).

On the other hand, \( \sigma \) in wet atmosphere is monotonically increased with increasing \( pO_2 \) at every temperature (Fig. 2b). In oxides, the proton dissolution can be described by following.

\[ V_0^{**} + H_2O + O_0^{*} \rightleftharpoons 2[OH_0^{*}] \quad \{K_4 = [OH_0^{*}]^2 [V_0^{**}]^{-1} pH_2O^{-1}\} \quad [4] \]
Here, interstitial protons OH°+. Due to the internal equilibrium of electron e' and hole h'

\[ e' + h^* = \text{null} \quad [K_e = \left[ h^* \right] \left[ e' \right]] \]  

The charge neutrality in major defects of apatite-type phase can be conducted as

\[ 2[V_\text{Ca}^{4+}] + [\text{OH}_\text{H}_2\text{O}]^+ + [h^*] = [e'] + 2[V_\text{Ca}^{3+}] \]  

\[ V_\text{Ca}'' \] calcium deficiencies. When the proton is dominant positive defect, the concentrations \[ [\text{OH}_\text{H}_2\text{O}]^+ \] are given by following:

\[ [\text{OH}_\text{H}_2\text{O}]^+ = 2[V_\text{Ca}^{3+}] + [e'] \]  

With this conditions, the hole concentration \[ [h^*] \] must be increased with increasing \( p_{\text{O}_2} \) according to Eq. 8 or 9.

\[ [h^*] = p_{\text{O}_2}^{1/2} K_4^{-1/4} (p_{\text{H}_2\text{O}} K_5)^{-1/4} \quad ([e'] \gg [V_\text{Ca}'']) \]  

\[ [h^*] = 2[V_\text{Ca}^{4+}] p_{\text{O}_2}^{1/2} K_4^{-1/2} (p_{\text{H}_2\text{O}} K_5)^{-1/2} \quad ([e'] \ll [V_\text{Ca}'']) \]  

However, the slope in log vs. log\( p_{\text{O}_2} \) plots of Cr-Ap is about 1/20 and this is much smaller than that for an electron hole conductor, i.e., \( p_{\text{O}_2}^{1/8} \) or \( p_{\text{O}_2}^{1/4} \) dependency, which is predicted from Eq. 8 or 9, respectively. This result shows that the transport number of hole might be not unity. Proton is speculated to be a feasible ionic carrier in Cr-Ap under the wet conditions.

To confirm the proton partial conductivity of Cr-Ap, the EMF measurements were conducted with the water vapor concentration cells (Fig. 3). Unfortunately, Cr-Ap is easily reduced under hydrogen-containing atmosphere and it is not suitable for the hydrogen concentration cell experiments. Figure 3a shows the cross-section SEM images of the disk prepared for the electrical conductivity measurements. The Cr-Ap particles of 100–1000 nm diameters are aggregated, and there exist pore spaces in the interior of the disk. Gas permeation test indicates that the physical leakage of gases through the disk is negligibly small. Accordingly, most of the pores do not penetrate from edge to edge in the disk.

The negative EMF is observed for the water vapor concentration cells with Cr-Ap electrolyte when the voltage at humidified side is measured relative to dried side. If Cr-Ap reveals proton conductivity, the following reactions must occur at Pt/Cr-Ap interfaces; wet side: \( 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \), and dry side: \( 4\text{H}^+ + \text{O}_2 + 4e^- \rightarrow 2\text{H}_2\text{O} \). Consequently, the EMF of the water concentration cell gives a negative sign in the current setup (Fig. 3b). The transport number of protons is estimated to be about 0.3 by Nernst relationship. On the other hand, the EMF of the oxygen concentration cell is nearly zero, disclosing that oxide ion transport number of Cr-Ap is negligibly small (Fig. 3b). Accordingly, it is concluded that Cr-Ap reveals proton and electron mixed conduction in wet oxidation atmosphere.

The proton transport might be feasible because some hydroxyl apatites exhibit proton conductivity by site-to-site proton hopping through the hydrogen bonded network in the lattice or through the surface hydroxyl groups. In the latter case, Ca(OH)₂ segregated to the surface is expected to contribute to the proton conductivity, but this phase is not thermodynamically stable at temperatures above 500°C even in humidified atmosphere. Hence it is clear that proton conductivity is characteristic of Cr-Ap. This is different from the previous report by Yasuda et al., in which electrical conduction of Cr-Ap was reported to be electronic nature even in wet atmosphere. Their conclusion was based on the observations that potential response against the current change was rapid. The DC polarization technique is not significant to demonstrate the ion-electron mixed conductivity.

Aoki et al reported that the highest occupied molecular orbital (HOMO) of \( \{\text{NdCrO}_3\} \) cluster is assigned to be d-characteristic and it tends to be spatially localized on the Cr atoms by ab initio MO calculation. If the HOMO largely contribute to the valence band of Cr-Ap, the hole conduction might occur through the variable-range hopping between \( \text{Cr}^{3+} \) and \( \text{Cr}^{5+} \) minor ions. The detail conduction mechanism will be reported in next paper.

Conclusions

In summary, it is demonstrated that Cr-Ap exhibits proton electron mixed conductivity in wet oxidation condition. The total electrical conductivities is in the order of \( 10^{-4} \) S cm⁻¹ between 800 and 900°C in the \( p_{\text{O}_2} \) range of more than \( 10^{-5} \) atm. These features must be related to the crystal structure of \( \text{MO}_4 \) oxometalate salt which allows proton incorporation by hydrogen bonding with \( \text{MO}_4 \) tetrahedra and the electronic properties of the tetrahedrally-coordinated \( \text{Cr}^{3+} \) ions with \( d^4 \) electron configuration. There exist oxometalate phases of \( \text{Cr}^{3+}, \text{Mn}^{4+}, \text{Fe}^{6+}, \text{V}^{4+} \) ions with \( d^0 \) or \( d^2 \) configuration. The current results encourage to explore the mixed ion-electron conductivity of these high oxidation state transition metal oxides.

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References