An Oxide Ion and Proton Co-Ion Conducting Sn_{0.9}In_{0.1}P_{2}O_{7} Electrolyte for Intermediate-Temperature Fuel Cells

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Abstract

The ionic conductivity of Sn_{0.9}In_{0.1}P_{2}O_{7} ceramic was investigated under various atmospheres within the temperature range of 130-230°C. Similar to mixed-conductive perovskite oxides at high temperatures (such as SrCe_{0.95}Yb_{0.05}O_{3-α}, La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-α} at 600-1000°C), Sn_{0.9}In_{0.1}P_{2}O_{7} can conduct both protons and oxide-ions at low temperatures (130-230°C). The conductivity of Sn_{0.9}In_{0.1}P_{2}O_{7} reaches 0.019 S/cm at 200°C in wet nitrogen. Its transport numbers determined by steam concentration cells are around 0.76 for proton and 0.12 for oxide-ion. The performance of direct methanol fuel cells at 170°C using mixed-ion conductive Sn_{0.9}In_{0.1}P_{2}O_{7} electrolyte is higher than that at 235°C using pure proton conductive CsH_{2}PO_{4} electrolyte. This is attributed to direct oxidation of CO at the anode by the oxide-ions generated at the cathode and moved through the Sn_{0.9}In_{0.1}P_{2}O_{7} electrolyte.

Introduction

Recently, intermediate temperature solid state fuel cells, which are operated in the temperature range of 150-300°C, attracted widespread interest because of their higher CO tolerance, faster electrochemical reaction kinetics and simpler thermal and water management as compared to proton exchange membrane fuel cells (PEMFCs). Since the working temperatures of intermediate temperature fuel cells (ITFCs) are lower than that of solid oxide fuel cells, ITFCs would allow the use of oxidation-resistant metallic alloys or even plastics as interconnect materials. It would also reduce the operating cost, increase the durability, extend the service life, and permit more frequent temperature and performance cycling [1-2].

Many anhydrous proton conductors have been investigated as the electrolytes for intermediate temperature H_{2}/O_{2} fuel cells, such as CsHSO_{4} [3], CsH_{2}PO_{4} [4-7], NH_{4}PO_{3}-based composites [8-13], Indium doped SnP_{2}O_{7} [14-16]. Although the CO tolerance of CsH_{2}PO_{4} fuel cells operating above 230°C, the transition temperature from a low- to a high-conductive phase, is much better than PEMFCs operating at 80°C, it is still lower than SOFCs because the hydrocarbon fuels can be directly electro-oxidized by the oxide ions in SOFCs [17, 18] and the operation temperatures (above 600°C) of SOFC are much higher than that of ITFCs. A method to enhance the CO tolerance of ITFCs is to use a proton and oxide ion co-ion conductive electrolyte membrane to replace the currently used proton conductive membrane. In such a cell, oxide ions are generated by the electrochemical reduction of dioxygen at the cathode and diffuse through the mixed oxide ion/proton membrane to the anode, where they may efficiently and directly oxidize any CO at the anode.

Most hydrocarbon oxidation reactions follow the Mars-van Krevelen mechanism [19-22] in which surface lattice O^{2-} is the actual oxidation agent. During these reactions, the O^{2-} reactant plays two important roles, i) being responsible for removal of H from C-H bonds to give water as in oxidative dehydrogenation, and ii) being capable of insertion into the intermediate complex to give the oxygenated product and water (mild oxidation). This mechanism is more efficient than that in the DMFC, in which methanol is directly electro-oxidized at low temperature by adsorbed hydroxide on a Pt-Ru electro-catalyst. It is the reason why an oxide-ion-conductive ceramic-supported Pt or Pt-Ru catalyst has a very
high CO oxidation ability, even at low temperatures provided an oxygen (or oxide ion) source is present. It has been reported that Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ ITFCs can tolerate up to 10% CO in H$_2$; i.e., 10% CO added to H$_2$ at anode did not decrease the performance of Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ ITFC at 250°C [14, 15]. The excellent CO tolerance at the anode for Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ ITFCs may attribute to the oxide ions transferring from the cathode through oxygen vacancies in Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ because of the existence of oxygen vacancies in Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ [14, 16].

In this work, the proton and oxide ion co-ion conductivity of Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ and the performance of Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ fuel cells with methanol and/or hydrogen fuel were investigated. A fuel cell using a co-ion conducting Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ membrane, operating at temperatures of 170-200°C, combined the advantages of both the SOFC and PEMFC, and complemented existing proton and oxide-ion fuel cell systems. The goal of introducing oxide ion transport in a proton conducting ceramic is to oxidize CO and methanol in an ITFC, which is different from prior works on mixed proton/oxide ion conducting perovskite oxides (such as SrCe$_{0.95}$Yb$_{0.05}$O$_3$$_\alpha$ [23], La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_3$$_\alpha$ [24]), for which proton conductivity is thermally activated at a lower temperature than that required for oxide ion conduction [25] and hence enables a lower SOFC operating temperature.

**Experimental**

In$^{3+}$-doped SnP$_2$O$_7$ was prepared using SnO$_2$ (Sigma-Aldrich 99.9%), In$_2$O$_3$ (Aldrich 99.99%) and H$_3$PO$_4$ (Fisher Scientific 85%) to form Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$. The starting materials were mixed and held with stirring at 300°C until the mixture formed a paste with a high viscosity. The pastes were calcined at 650°C for 2.5 hours and then ground into powders with a mortar and pestle. The compound was pressed at 250MPa into pellets and then coated with Ag for conductivity measurement and with Pt catalyst for fuel cell testing. The pellets were 13 mm in diameter and around 0.8 mm in thickness. For comparison, CsH$_2$PO$_4$ was also prepared as described in [4] using Cs$_2$CO$_3$ (Sigma-Aldrich 99%) and H$_3$PO$_4$ (Fisher Scientific 85%) as precursors. The crystalline structure of the compounds was analyzed by X-ray diffraction (PANalytical X’Pert Pro MPD diffractometer with Cu radiation) and the micro-morphology of the powders and pellets was observed by scanning electron microscopy (SEM) images using a FEI Quanta 200 with Electron Diffraction Spectrometer (EDS).

Both the anode and cathode contained two overlapped conductive porous layers: a diffusion layer and a catalyst layer. The diffusion layer was formed from carbon cloth (E-TEK, B1A) which was smoothed by coating a mixture of 85 wt.% carbon powder (Vulcan XC72) and 15 wt.% polytetrafluoroethylene (PTFE, Aldrich, 60% dispersion). The carbon powder loading was 2 mg/cm$^2$. The catalyst layer was formed from either Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ or CsH$_2$PO$_4$ (35wt.%), 40wt.% Pt/C catalyst (50wt.%, E-TEK) and PTFE (15 wt.%). The catalyst ink was prepared by mixing Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ (or CsH$_2$PO$_4$), distilled water, Pt/C catalyst, isopropanol (Fisher Scientific, 99.9%) and PTFE. The ink was brushed onto the diffusion layer and dried to form an electrode (anode or cathode). The platinum loading was 4 mg/cm$^2$. The electrolyte membrane (Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ or CsH$_2$PO$_4$) was sandwiched by the anode and cathode to form a single cell. Humidification of gas was achieved by saturating nitrogen/hydrogen/oxygen with water at a given temperature, resulting in a given water partial pressure, such as 76°C for 40% H$_2$O. In order to add methanol into fuel gases, hydrogen/nitrogen was saturated with a mixture of methanol and water at a given temperature.

Conductivity measurements were carried out using a Salartron (SI1287 and SI1260) electrochemical impedance system in the frequency range of 0.001-10$^6$ Hz. At each temperature, the sample was held about 30 minutes prior to measurement.

**Results and discussions**

Figure 1 shows typical XRD patterns for Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ and CsH$_2$PO$_4$ at room temperature. The peaks observed are identical to those reported in PDF# 00-29-1352 (SnP$_2$O$_7$) and PDF# 00-35-0746
(CsH₂PO₄). SnP₂O₇ doped with 10% In³⁺ showed the same structure as the undoped SnP₂O₇, characterized by a cubic or pseudo-cubic structure with SnO₆ octahedral at the corners and P₂O₇ units at the edges [26]. However, M. Nagao et al. reported that 10% In³⁺ doping increased the lattice constant from 7.945 Å to 7.950 Å [16] and created oxygen vacancy defects [14, 16]. And the chemical composition of Sn₀.₉In₀.₁P₂O₇ was confirmed by Energy Dispersive Analysis of X-rays (EDAX). All peaks in Figure 1b could be indexed to CsH₂PO₄, indicating the synthesized material is pure CsH₂PO₄.

Figure 2 shows the morphologies of powders and morphologies of cross-sections for Sn₀.₉In₀.₁P₂O₇ and CsH₂PO₄ pellets. The cross-sections were obtained by cutting the pellets with a sharp blade. Although the particle size of Sn₀.₉In₀.₁P₂O₇ is smaller than that of CsH₂PO₄ (Figures 2a and b), the porosity of the former is higher than the latter, i.e., the density of the CsH₂PO₄ pellet is higher than that of Sn₀.₉In₀.₁P₂O₇ (Figures 2c and d).

Figure 3 shows the conductivities of Sn₀.₉In₀.₁P₂O₇ and CsH₂PO₄ at different temperatures in humidified nitrogen. The conductivity of Sn₀.₉In₀.₁P₂O₇ continuously increased with increasing water vapor pressure from 3.2 to 40% (Fig. 3a). The conduction behavior of Sn₀.₉In₀.₁P₂O₇ at different temperatures is different from superprotonic character of CsH₂PO₄ that shows a sharp increase in the conductivity of a few orders of magnitude by a structural transition from a low- to a high-temperature phase (Fig. 3). The maximum protonic conductivities of Sn₀.₉In₀.₁P₂O₇, achieved at around 200°C in 40% H₂O, is 0.019 S/cm, which is similar to that (0.02 S/cm) of CsH₂PO₄ at 240°C. The thermal variations of proton conductivities for Sn₀.₉In₀.₁P₂O₇ and CsH₂PO₄ were consistent with reported results [4, 14], although the conductivity of Sn₀.₉In₀.₁P₂O₇ is slightly lower than reported values [14]. The reason why the conductivity decreases after 200°C is not clear. It cannot be attributed to the escape of water produced by the reversal of reaction 1 because the evolution of water vapor from Sn₀.₉In₀.₁P₂O₇ starts above 260°C [16]. If it is due to the escape of water, the peak position should not be fixed at 200°C but move to a higher temperature with higher water partial pressure.

The interaction (reaction 1) between water vapor and oxygen vacancies (and/or electron holes) may be responsible for...
protonic conduction in Sn_{0.9}In_{0.1}P_{2}O_{7} [14, 16], which is similar to the mechanism of proton incorporation in perovskite oxides such as SrCe_{0.95}Yb_{0.05}O_{3-δ}. The increase in conductivity of Sn_{0.9}In_{0.1}P_{2}O_{7} with humidity (Fig. 3) supports the hypothesis of the proton conducting mechanism. During the operation of fuel cells, protons generated at anode (reaction 2) move through the Sn_{0.9}In_{0.1}P_{2}O_{7} membrane to cathode to react with oxygen (reaction 3), whereas oxide ions transits in the opposite direction from cathode (reaction 4) to anode to oxidize the CO or CH_{3}OH (reaction 5). CO and methanol can also be chemically oxidized with water through water-gas-shift reaction (reaction 6) and reforming (reaction 7) at intermediate temperatures.

Proton conduction in Sn_{0.9}In_{0.1}P_{2}O_{7}

\[ H_{2}O(g) + V_{O}^{**} \rightarrow 2H^{+} + O_{2}^{••} \]

and/or \[ H_{2}O(g) + 2H^{+} \rightarrow 2H_{2}^{+} + \frac{1}{2}O_{2} \]  \hspace{1cm} (1)

Anode reaction in Sn_{0.9}In_{0.1}P_{2}O_{7} fuel cells

\[ H_{2} \rightarrow 2H^{+} + 2e^{-} \]  \hspace{1cm} (2)

Cathode reaction in Sn_{0.9}In_{0.1}P_{2}O_{7} fuel cells

\[ \frac{1}{2}O_{2} + 2H_{2}^{+} + 2e^{-} \rightarrow H_{2}O \]  \hspace{1cm} (3)

Oxide ion conduction in Sn_{0.9}In_{0.1}P_{2}O_{7}

\[ \frac{1}{2}O_{2} + V_{O}^{**} + 2e^{-} \rightarrow O_{2}^{••} \]  \hspace{1cm} (4)

Direct CO and methanol oxidation by oxide ion in anode

\[ O_{2}^{••} + [R] \rightarrow V_{O}^{**} + [P] + 2e^{-} \]  \hspace{1cm} (5)

CO oxidation in anode through water-gas-shift reaction

\[ H_{2}O + CO \rightarrow CO_{2} + H_{2} \]  \hspace{1cm} (6)

CH_{3}OH oxidation in anode through reforming

\[ CH_{3}OH + H_{2}O \rightarrow CO_{2} + 3H_{2} \]  \hspace{1cm} (7)

Here, \( h^{+}, H^{+}, V_{O}^{**}, O_{2}^{••}, [R], [P] \) and \( e^{-} \) denote an electron hole, a proton, an oxygen vacancy, a lattice oxide ion, reductant (CO and CH_{3}OH), reduction product and an electron, respectively.

Another possibility for proton conduction in Sn_{0.9}In_{0.1}P_{2}O_{7} is the residual phosphoric acid on the surface of material. If phosphoric acid exists on the surface of material, it should be dissolved into water when the Sn_{0.9}In_{0.1}P_{2}O_{7} particles are soaked in the water, thus the washed Sn_{0.9}In_{0.1}P_{2}O_{7} should have lower conductivity than that of unwashed Sn_{0.9}In_{0.1}P_{2}O_{7}. However, the conductivity of washed Sn_{0.9}In_{0.1}P_{2}O_{7} shows similar conductivity with unwashed one, indicating that proton conduct in Sn_{0.9}In_{0.1}P_{2}O_{7} is mainly through water- oxygen vacancy reaction. More experiments are still needed to elucidate the exact role of residual phosphoric acid in proton conduction of Sn_{0.9}In_{0.1}P_{2}O_{7} if it exists.

To check the conductivity of Sn_{0.9}In_{0.1}P_{2}O_{7} electrolyte in fuel cells, the impedances of Sn_{0.9}In_{0.1}P_{2}O_{7} membranes were measured in O_{2} and N_{2} with and without the presence of water (Fig. 4). Comparing the impedances of Sn_{0.9}In_{0.1}P_{2}O_{7} measured in dry N_{2} and dry O_{2} (Fig. 4a). The low-frequency-line did not intersect the real axis, which indicates that Sn_{0.9}In_{0.1}P_{2}O_{7} is an electronic insulator. Adding water to oxygen gas results in an even lower electronic conductivity, as evidenced by almost straight line in the low frequency region (Fig. 4b). Fig. 4 clearly demonstrated that Sn_{0.9}In_{0.1}P_{2}O_{7} is an electronic insulator at temperatures below 200°C whether in a dry or wet atmosphere.

The maximum protonic conductivities of 0.019 S/cm is achieved at around 200°C in 40% H_{2}O. To avoid the conductivity drop, the Sn_{0.9}In_{0.1}P_{2}O_{7} membranes and Sn_{0.9}In_{0.1}P_{2}O_{7} fuel cells were tested at 170°C (i.e., below 200°C). Figure 5 shows the time dependence of conductivity of Sn_{0.9}In_{0.1}P_{2}O_{7} at 170°C and CsH_{2}PO_{4} at 235°C in wet nitrogen with 40% water vapor. It is clear that the conductivities of
both Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ and CsH$_2$PO$_4$ are very stable. Therefore, both Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ and CsH$_2$PO$_4$ are suitable electrolytes for intermediate temperature fuel cells.

Based on reactions 1 and 4, Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ should be a mixed proton and oxide ion conductor in humidified gas. In order to confirm Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ is a mixed-conducting conductor under humidified conditions, the transport numbers of protons and oxide ions were determined by measuring the electromotive force, EMF, of steam concentration cells H$_2$/O$_2$ ($P_{H_2O}$ = 0.6KPa), Pt/C/Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$/Pt/C, H$_2$/O$_2$ ($P_{H_2O}$ = 3.2KPa). The Nernst potential of the steam concentration cell can be determined by the following equations [28]:

$$E_0 = (RT / 4F)[t_{ion} \ln(P_{H_2}^{II} / P_{O_2}^{II}) - 2t_{H^+} \ln(P_{H_2O}^{II} / P_{H_2O}^{II})]$$  \hspace{1cm} (8)

where $t_{ion} = t_{H^+} + t_{O^2^-}$ is the ionic transport number and the carrying gas is oxygen. Or

$$E_0 = (RT / 2F)[-t_{ion} \ln(P_{H_2}^{II} / P_{H_2}^{II}) + t_{O^2^-} \ln(P_{H_2O}^{II} / P_{H_2O}^{II})]$$  \hspace{1cm} (9)

where the carrying gas is hydrogen.

Since the pressures of the carrying gases (oxygen) at the both sides of the steam concentration cell are very close and transport number for protons is larger than that for oxide ions (i.e. $2t_{H^+} >> t_{H^+} + t_{O^2^-}$), the first parts of equations (8) are negligible. Therefore, the equations (8) can be expressed as: $E_0 = -t_{H^+} (RT / 2F) \ln(P_{H_2O}^{II} / P_{H_2O}^{II})$, and the proton transport number, $t_{H^+}$, can be calculated from the measured $E_0$, $t_{H^+} = E_0 / E_{th}$ [29]. Here $E_{th} = (RT / 2F) \ln(P_{H_2O}^{II} / P_{H_2O}^{II})$ is defined as the theoretical EMF. As shown in Figure 6a, the proton transport numbers are 0.7-0.8 (average 0.76), depending on the temperatures. After switching the carrying gas from oxygen to hydrogen, the oxygen-ion transport number $t_{O^2^-}$ at different temperatures can be calculated from equation (9) using the measured $E_0$ values and calculated proton transport numbers at the same temperatures. As shown in Figure 6b, the oxygen-ion transport numbers are around 0.12. The total ionic transport number (0.88) of Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ is less than unity, which is probably attributed to gas leakage in the steam concentration cells due to the low density of the membrane (Figure 2). The gas leakage will result in a lower measured EMF than the theoretical value, and less than unity for the total ionic transport numbers. The conductivity of oxide ions in Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ at 200°C is around 10$^{-3}$ S/cm, which is close to the oxide ion conductivities of La$_0.8$Sr$_0.2$Ga$_0.8$Mg$_0.2$ (LSGM) [30] and Bi$_2$TiO$_2$V$_{1.8}$O$_{10.7}$ [31] at 250°C.

The carbon monoxide generated by reforming reaction would dilute the hydrogen fuel and/or poison the catalyst in anode even at intermediate temperature and make fuel cell performance worse. Since Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ is a proton and oxide ion co-ion conductor and
the oxide ion will oxidize the CO (reaction 5 can be particularized as \( O^+_O + CO \rightarrow V^{**}_O + CO_2 + 2e^- \)), the exhaust CO can become as a fuel in the direct methanol \( Sn_{0.9}In_{0.1}P_2O_7 \) fuel cells, and thus the direct methanol \( Sn_{0.9}In_{0.1}P_2O_7 \) fuel cells should perform better than direct methanol \( CsH_2PO_4 \) fuel cells.

To test the capability of direct oxidation of CO by oxide ions, the performance of a Pt/C fuel cell using a mixed proton/oxide ion conducting \( Sn_{0.9}In_{0.1}P_2O_7 \) electrolyte was investigated in the temperature range 130-170°C and compared with a fuel cell using a pure proton conductor \( CsH_2PO_4 \) electrolyte at 235°C. Cell voltages and power densities of two cells are shown in Figures 7 and 8 as a function of current density. As expected, the power density of the \( Sn_{0.9}In_{0.1}P_2O_7 \) fuel cell increased with temperature and the maximum power densities at 170°C were 14.7mW/cm² for hydrogen, 14.9mW/cm² for a mixture of hydrogen and methanol and 4.0mW/cm² for methanol. Due to the fast reaction kinetics at a comparatively high operating temperature (235°C) for the \( CsH_2PO_4 \) fuel cell, the maximum power density (17.3mW/cm²) of the H₂/O₂ \( CsH_2PO_4 \) fuel cell was slightly higher than the H₂/O₂ \( Sn_{0.9}In_{0.1}P_2O_7 \) fuel cell, even though the ionic conductivities of the two electrolytes are very close. However, the power densities of the \( CsH_2PO_4 \) fuel cell at 235°C using hydrogen-methanol (13.7mW/cm²) and methanol (2.1mW/cm²) were much lower than that of the \( Sn_{0.9}In_{0.1}P_2O_7 \) fuel cell at 170°C. When 15% methanol was added into hydrogen, the power density of the \( CsH_2PO_4 \) fuel cell lost 21% power density, decreasing from 17.3mW/cm² to 13.7mW/cm², but the power density of the \( Sn_{0.9}In_{0.1}P_2O_7 \) fuel cell remained the same. When the fuel was switched from the H₂-CH₃OH mixture to pure methanol, the power density for the \( CsH_2PO_4 \) fuel cell had an 85% drop, from 13.7mW/cm² to 2.1mW/cm², while the drop for the \( Sn_{0.9}In_{0.1}P_2O_7 \) fuel cell was only 75%, from 14.9mW/cm² to 4.0mW/cm². Since both the amount of platinum loading in two fuel cell cells and ionic conductivity of two electrolytes (\( CsH_2PO_4 \) and \( Sn_{0.9}In_{0.1}P_2O_7 \)) were the same, even the \( CsH_2PO_4 \) cell has faster electrochemical reaction kinetics than that of the \( Sn_{0.9}In_{0.1}P_2O_7 \) cell because of its higher operation temperature, the difference in performance must come from the electrolytes. The higher performance of methanol fuel cells using \( Sn_{0.9}In_{0.1}P_2O_7 \) as an electrolyte at 170°C compared to using a \( CsH_2PO_4 \) electrolyte at 235°C strongly indicated that CO was effectively oxidized by the oxide ions, resulting in enhancement of the fuel cell performance.

Although the \( CsH_2PO_4 \) fuel cell has a lower power density than the \( Sn_{0.9}In_{0.1}P_2O_7 \) fuel cell when methanol is present in the fuel, its open circuit voltage is higher. This is due to the higher density of the \( CsH_2PO_4 \) membrane as shown in Figure 2, and the higher density may be another reason that the power density of \( CsH_2PO_4 \) is higher than \( Sn_{0.9}In_{0.1}P_2O_7 \) in a H₂/O₂ fuel cell, even though they have very similar conductivities.
Conclusions

A proton and oxide ion co-ion conductor, Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$, was synthesized and characterized. The conductivity of Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ and performance of Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ membrane fuel cell were investigated under various atmospheres in the temperature range of 130-230°C and compared with pure proton conductive CsH$_2$PO$_4$ and CsH$_2$PO$_4$ membrane fuel cells. The conductivity of Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ reached 0.019 S/cm at 200°C in wet nitrogen, and the transport numbers determined by steam concentration cells were 0.76 for protons and 0.12 for oxide ions. The higher performance of a methanol Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ fuel cell at 170°C compared to a methanol CsH$_2$PO$_4$ fuel cell at 235°C was attributed to the direct oxidation of CO at the anode by the oxide ions transported through the Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ electrolyte. Due to the unique concept of oxidation of CO by oxide ion transported from the cathode, and preliminary results on a co-ion (proton/oxide ion) conductive fuel cell with methanol fuel, the co-ion conducting membrane fuel cell, operating at around 200°C, may be the next-generation methanol fuel cell and reforming fuel cell because it combines the advantages of both SOFC and PEMFC.

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