Direct Ethanol Fuel Cell Using Hydrotalcite Clay as a Hydroxide Ion Conductive Electrolyte

By *Kiyoharu Tadanaga,* Yoshihiro Furukawa, Akitoshi Hayashi,* and *Masahiro Tatsumisago*

Great efforts have been devoted to the design and development of polymer electrolyte fuel cells and direct methanol fuel cells as new power sources. Nevertheless, the practical use of such fuel cells remains hindered by high costs, including costs for Pt-based catalysts and electrolyte membranes. Furthermore, the toxic properties of methanol present a severe problem. Consequently, direct ethanol fuel cells (DEFCs) have attracted much attention recently. Here we propose an alkaline-type DEFC using a natural clay electrolyte with nonplatinum catalysts. So-called hydrotalcite clay, Mg–Al layered double hydroxide intercalated with CO_3^{2-} (Mg–Al CO_3^{2-} LDH), was shown to be a hydroxide ion conductor. An alkaline-type DEFC using this natural clay as the electrolyte and aqueous solution of ethanol and potassium hydroxide as a source of fuel exhibits excellent electrochemical performance from room temperature to 80 °C: open circuit voltage of 0.87 V and electric power of more than 65 mW cm^{-2} were obtained. The environmentally friendly DEFC proposed herein offers superior safety, cost, material, and stability.

Polymer electrolyte fuel cells (PEFCs) have been studied extensively for use as a new energy source. Furthermore, direct alcohol fuel cells (DAFCs) are anticipated for use as energy sources of portable devices such as laptop computers and mobile phones.[1,2] Direct methanol fuel cells (DMFCs) with proton conductive membranes have been studied mainly as DAFCs to date, but their performance is inferior to that of PEFCs using a proton conductive membrane and pure hydrogen because of high overpotential for methanol oxidation and crossover of methanol in the membrane.[1,2] The DMFCs using alkaline anion exchange membranes, which present advantages in methanol oxidation and methanol crossover, are very attractive. Recently, studies of alkaline type fuel cells are increasing.[1–8]

For the practical use of fuel cells for portable devices, toxic properties of methanol present a severe problem. For that reason, direct ethanol fuel cells (DEFCs) have been attracting much attention recently.[7,8] Relatively safe ethanol is producible using biomass. Both proton conductive organic polymer membrane and anion exchange organic polymer membranes have been used as electrolytes for DEFCs. Because the use of noble platinum is the most daunting hurdle for the commercialization of PEFCs and because the oxidation reaction is faster than those of acid-type fuel cells, an alkaline type direct ethanol fuel cell with a nonplatinum catalyst[1] is attractive. However, like traditional aqueous KOH electrolyte alkaline fuel cells, the formation of carbonate precipitation will occur in an ethanol solution containing alkaline metal hydroxide. Consequently, development of an electrolyte that will not be degraded with formation of carbonate is desired.

Regarding the operation of temperature of fuel cells including PEFCs, operation of fuel cells at temperatures higher than 80 °C presents many advantages[9,10]; many research groups, including our own, have proposed strong solid acid type proton-conductive inorganic-based materials as electrolytes of intermediate temperature fuel cells[9–14] However, for such strong acids, electrode materials that are useful without corrosion are difficult to find. Consequently, alkaline type fuel cells are attractive from the viewpoint of high-temperature operation.

Hydrotalcite-type clays (or layered double hydroxides)[15,16] are a family of anionic clays with a layered structure and the general formula $[M^{2+}_{1-x}M^{3+}_x (OH)_2] [A_{n-x/n} \cdot zH_2O]$. They consist of hydroxides of common and abundant metals such as magnesium and aluminum; they can be synthesized at ambient temperature and pressure. The host layers are charged positively by replacement of divalent metal cations with trivalent ones. The positive charge is compensated by interlayer anions. The interlayer anions are exchangeable; inserting various anions into interlayers (intercalation) can give hydrotalcites new functions.[15,16] To date, clay minerals have been used only as fillers for proton conductive membranes or proton conductors,[17–19] but have been considered neither as hydroxide anion conductors nor as fuel cell electrolytes. Recently, we examined the ionic conductivity for Mg–Al layered double hydroxides (LDHs) intercalated with several inorganic anions,[20] reporting that they have high ionic conductivity under 80% relative humidity. In addition to high ionic conductivity, Mg–Al LDH is very stable in alkaline solution because Mg–Al LDHs were prepared by precipitation under a basic condition. Therefore, we have devoted attention to the application of Mg–Al LDH as an electrolyte of alkaline-type fuel cells.

This study investigated ionic conductivity and conducting ionic species of Mg–Al CO_3^{2-} LDH, which occurs as a natural mineral. We show that a direct ethanol fuel cell with Mg–Al CO_3^{2-} LDH as the electrolyte and nonplatinum catalysts, operating at room temperature to 80 °C, exhibits excellent electrochemical performance: open circuit voltage of 0.87 V and electric power of more than 65 mW cm^{-2} were obtained.

The Cu Kα XRD pattern of the precipitates prepared using the coprecipitation method from a mixture of $Mg(NO_3)_2$ and $Al(NO_3)_3$ aqueous solution and Na_2CO_3 solution exhibited typical reflections of a layered structure at $2\theta = 11.42°$ and $22.88°$, respectively. The basal spacing calculated using those peaks agrees with the Mg–Al LDHs intercalated with CO_3^{2-}.[21,22]

[*] Dr. K. Tadanaga, Y. Furukawa, Dr. A. Hayashi, Prof. M. Tatsumisago
Department of Applied Chemistry
Graduate School of Engineering
Osaka Prefecture University
Sakai, Osaka 599-8531 (Japan)
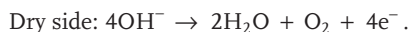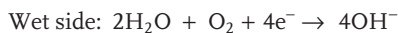E-mail: tadanaga@chem.osakafu-u.ac.jp

Fourier transform (FT)-IR and ion chromatography measurements also verified that the obtained Mg–Al LDHs were intercalated with CO_3^{2-}. Electrical properties of Mg–Al LDHs were determined using ac impedance spectroscopy. The resultant Z″ vs. Z′ plot showed that Mg–Al LDHs were ionic conductors.

Figure 1 presents the relative humidity (RH) dependence of conductivities of Mg–Al LDH intercalated with CO_3^{2-} (Mg–Al CO_3^{2-} LDH) at 60, 70, and 80 °C. The conductivities of Mg–Al CO_3^{2-} LDH increase with an increase in RH and temperature, and reached 3.3×10^{-3} S cm^{-1} at 80 °C under RH = 85%. These results indicate that the amount of adsorbed water in Mg–Al LDH must increase with increased RH, and that the adsorbed water contributes to increased conductivity.

The conducting ion species was investigated using the concentration cell with water vapor. Variations of electromotive force (EMF) for the water vapor concentration cells using anion exchange membrane, Mg–Al CO_3^{2-} LDH, and cation exchange membrane are portrayed in **Figure 2**. The negative EMF is observed for the concentration cells using Mg–Al CO_3^{2-} LDH and the anion exchange membrane, whereas positive EMF is observed for the concentration cell using the cation exchange membrane. The reaction at the electrode can be described as follows. For the proton conductor:

Wet side: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Dry side: $4H^+ + O_2 + 4e^- \rightarrow 2H_2O$
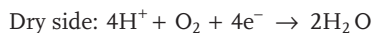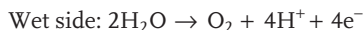
For the anion (OH$^-$) conductor:

Wet side: $2H_2O + O_2 + 4e^- \rightarrow 4OH^-$

Dry side: $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$.

Consequently, the EMF of the water vapor concentration cell gives a reverse sign between the proton conductor and anion

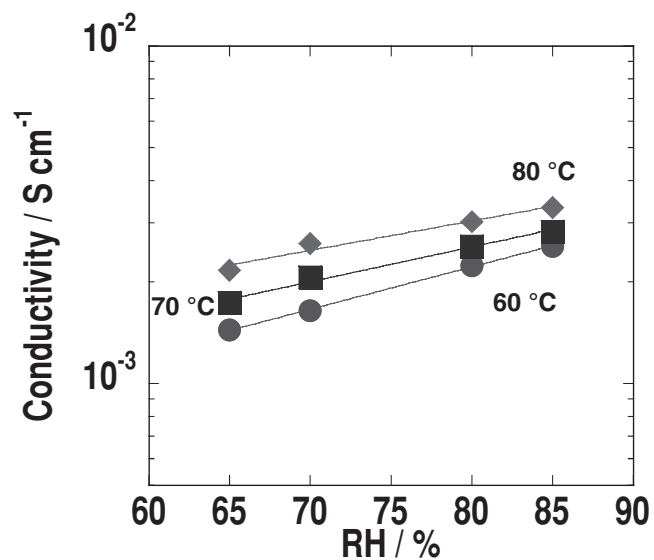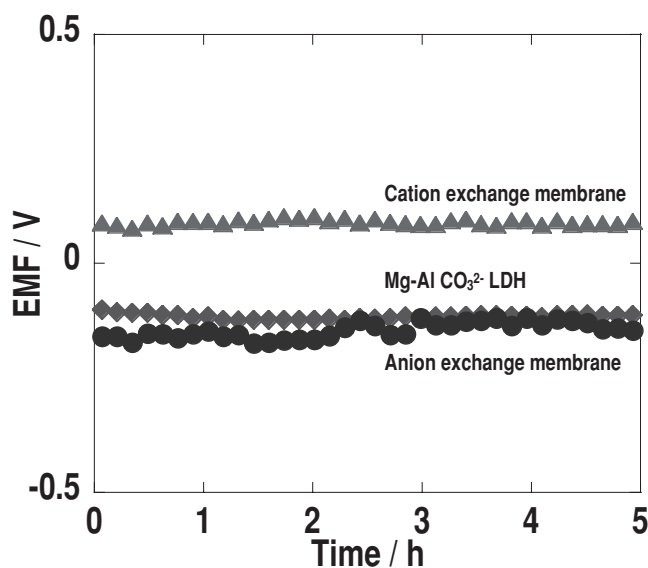**Figure 2.** Variation of EMF for the water vapor concentration cells using anion exchange membrane, Mg–Al CO_3^{2-} LDH, and cation exchange membrane.

(hydroxide ion) conductor. Figure 1 shows that water takes important roles in ion conduction of Mg–Al CO_3^{2-} LDH. The relative humidity dependence of conductivity and the results in EMF measurements show that the predominant conducting ion species of Mg–Al CO_3^{2-} LDH are hydroxide ions under humidified conditions. Roy and Besse clarified that Zn-Cr LDH intercalated with Cl$^-$ ions is a proton conductor using a hydrogen concentration cell.[17] They pointed out that the influence of the nature of cations in the main sheets must be correlated to acid-basic properties of hydroxyl groups. Not many studies of ionic conduction of LDHs have been reported, and the influence of cations to the ionic conduction in LDH has not been clarified yet. However, here we show that Mg–Al LDH, where Mg is a basic element, is a hydroxide conductor under humid conditions.

Figure 3 shows the cell voltage and power density versus current density for a passive-type DEFC with Mg–Al CO_3^{2-} LDH as an electrolyte and nonplatinum catalysts, at room temperature, 40, 60 and 80 °C. The open circuit voltage of the cell is about 0.87 V, indicating that crossover of ethanol to the cathode side is sufficiently small for fuel cell operation. The cells work as a DEFC; the larger current density is observed at higher temperatures. The maximum power density of 65 mW cm^{-2} is obtained for the cell at 80 °C, which is comparable to that of an active-type DEFC using those nonplatinum catalysts and an anion-exchange membrane[23] or a passive DEFC using Pd/MWCNT anode catalyst and the nonplatinum cathode catalyst used in this study with an anion-exchange membrane.[24] The superior performances at higher temperatures must be caused by the increase in ionic conductivity with an increase in temperature, as presented in Figure 1. The ac impedance measurements of the cell under the operation also suggest that the resistance of the electrolyte decreased with an increase in temperature. Reactions at the cathode and anode must also be accelerated
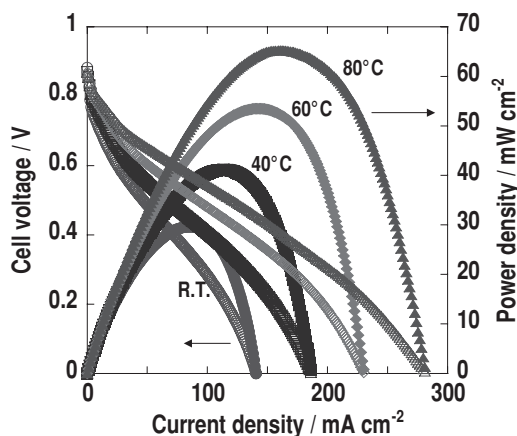

Figure 1. Ionic conductivity of Mg–Al CO_3^{2-} LDH at 60 (circle), 70 (square), and 80 °C (diamond).

Figure 3. Performance of the DEFC using Mg–Al CO$_3^{2-}$ LDH at various temperatures.

with an increase in temperature. We also confirmed that the DEFC using fuel with a lower KOH concentration or that without KOH also worked (see the Supporting Information). However the obtained power density was decreased with a decrease in KOH concentration. The resistance of the electrolyte slightly decreased with KOH concentration. In the anode electrode composed of the catalyst on carbon with carbon cloth, no ionomer was used, and the electrode was only attached to the pelletized Mg–Al CO$_3^{2-}$ LDH powder. Thus, KOH in the fuel must act as ionic link between the electrode and the Mg–Al CO$_3^{2-}$ LDH, and play an important role for acceleration of the reaction at the anode catalyst, while KOH in the fuel also slightly increased the ionic conductivity of the solid electrolyte. Characterization of the catalyst/carbon/solid electrolyte interfaces in the present electrodes and construction of better catalyst/carbon/solid electrolyte interfaces should be further investigated to improve the fuel cell performance and to reduce the use of KOH in fuel.

For the practical use of fuel cells, PEFC still presents high costs, including those of the Pt catalyst and electrolyte membrane. The direct ethanol fuel cell that we proposed herein uses "natural clay" as the electrolyte; nonplatinum catalysts are used. In alkaline fuel cells of this type, the metal cations react with dissolved CO$_2$ in alcohol fuels producing metal carbonate precipitates that decrease the fuel cell performance. However, the electrolyte is carbonate salt. For that reason, effects of carbonate precipitate formation in the fuel must be very small. In addition, the inorganic materials must present great advantages for long-term stability during use as the electrolyte of fuel cells. The cell performances in this study show the high potential of the Mg–Al CO$_3^{2-}$ LDH as an electrolyte for alkaline-type DEFC at temperatures higher than 80 °C. Therefore, we believe that the alkaline-type DEFC proposed herein will open new vistas for fuel cell development.

In conclusion, results show that Mg–Al CO$_3^{2-}$ LDH, known as hydrotalcite clay, functions as an electrolyte for alkaline type direct ethanol fuel cells. The EMF measurements for the water vapor concentration cell using Mg–Al CO$_3^{2-}$ LDH showed that Mg–Al CO$_3^{2-}$ LDH is a hydroxide ion conductor under the humidified condition. The alkaline type DEFC using Mg–Al CO$_3^{2-}$ LDH as the electrolyte in this study exhibited promising electrochemical performance.

Experimental Section

Using the co-precipitation method, Mg–Al LDH intercalated with CO$_3^{2-}$ (Mg–Al CO$_3^{2-}$ LDH) was prepared.[20] A mixture of Mg(NO$_3$)$_2$ and Al(NO$_3$)$_3$ aqueous solution with Mg/Al = 3 was added to Na$_2$CO$_3$ solution with stirring at 80 °C. The pH of the reaction mixture was adjusted to 10 by dropwise addition of NaOH solution and the reaction mixture was aged at 80 °C for 17 h. The precipitates were filtered, washed with water, and dried at 80 °C for 24 h.

Electrical conductivities of the pellets obtained by cold pressing under a pressure of 360 MPa were measured: the diameters and thickness of the pellets were 10 mm and about 0.5 mm, respectively, and the estimated relative density of the pellet was more than 90%. Gold was evaporated on both sides of the pellets as the electrodes. The conductivity of the pellets was determined from impedance data obtained using an impedance analyzer (Solartron 1260; Solartron Analytical) at frequencies from 10 Hz to 8 MHz.

The conducting ion species was investigated using a water vapor concentration cell. Pelletized Mg–Al CO$_3^{2-}$ LDH powder, an anion exchange membrane (A202; Tokuyama Corp.) and a cation exchange membrane (Nafion 117; DuPont) were used as the electrolyte. The membranes or pelletized Mg–Al CO$_3^{2-}$ LDH were sandwiched with a pair of the Pt-loaded carbon sheets. The electromotive force (EMF) of a cell with the electrolyte sandwiched with carbon sheets was measured at 30 °C by exposing a flow of humidified N$_2$/O$_2$ gas to one side of the cell and dried N$_2$/O$_2$ gas to the other side.

A passive-type direct ethanol fuel cell was fabricated using pelletized Mg–Al CO$_3^{2-}$ LDH powder as electrolyte (thickness of the pellet was about 0.3 mm). The anode and cathode electrodes with non-Pt catalysts (Hypermec; ACTA S.p.A.) were used, where Ni–Co-based alloy on carbon powder is used for the anode and Fe–Co-based alloy on carbon powder is used for the cathode.[23] The cathode and anode backing layers were nickel form and carbon cloth, respectively. Performance of an active-type DEFC using those electrodes with the nonplatinum catalysts and an anion-exchange membrane has already been reported.[23] The pelletized Mg–Al CO$_3^{2-}$ LDH was sandwiched with the two electrodes and the gold-plated current collectors that were attached with cell fixtures. An aqueous solution of ethanol and potassium hydroxide (10 wt% EtOH-10 wt% KOH) was used as fuel. The volume of the anode compartment was about 25 cm^3 and the cathode was exposed to air. The active area of the cell was about 0.4 cm.^{2} Polarization performances were measured using a potentiostat and galvanostats (Autolab, PGSTAT30) at R.T.–80 °C.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

[1] C. Bianchini, P. K. Shen, *Chem. Rev.* **2009**, *109*, 4183.

[2] J. R. Varcoe, R. C. T. Slade, *Fuel Cells* **2005**. *5*, 187.

[3] J. R. Varcoe, R. C. T. Slade, E. L. H. Yee, *Chem. Commun.* **2006**, 1428.

[4] E. Agel, J. Bouet, J. F. Fauvarque, *J. Power Sources* **2001**, *101*, 267.

[5] Z. Ogumi, K. Matsuoka. S. Chiba, M. Matsuoka, Y. Iriyama, T. Abe, M. Inaba, *Electrochemistry* **2002**, *70*, 980.

[6] K. Matsuoka, Y. Iriyama, T. Abe, M. Matsuoka, Z. Ogumi, *J. Power Sources* **2007**, *150*, 27.

[7] A. Kowal, M. Li, M. Shao, K. Sasaki, M. B. Vukmirovic, J. Zhang, N. S. Marinkovic, P. Liu, A. I. Frenkel, R. R. Adzic, *Nat. Mater.* **2009**, *8*, 325.

[8] N. Fujiwara, Z. Siroma, S. Yamazaki, T. Ioroi, H. Senoh, K. Yasuda, *J. Power Sources* **2008**, *185*, 621.

[9] Q. Li, R. He, J. O. Jensen, N. J. Bjerrum, *Chem. Mater.* **2003**, *15*, 4896.

[10] J. Zhang, Z. Xie, J. Zhang, Y. Tang, C. Song, T. Navessin, Z. Shi, D. Song, H. Wang, D. P. Wilkinson, Z. Liu, S. Holdcroft, *J. Power Sources* **2006**, *160*, 872.

[11] S. M. Haile, D. A. Boysen C. R. I. Chisholm, R. B. Merie, *Nature* **2001**. *410*, 910.

[12] K. Tadanaga, H. Yoshida, A. Matsuda, T. Minami, M. Tatsumisago, *Chem. Mater.* **2003**, *15*, 1910.

[13] K. Tadanaga, H. Yoshida, A. Matsuda, T. Minami, M. Tatsumisago, *Electrochim. Acta* **2004**, *50*, 705.

[14] T. Tezuka, K. Tadanaga, A. Hayashi, M. Tatsumisago, *J. Am. Chem. Soc.* **2006**, *128*, 16470.

[15] A. I. Khan, D. O'Hare, *J. Mater. Chem.* **2002**, *12*, 3191.

[16] D. G. Evans, X. Duan, *Chem. Comm.* **2006**, 485.

[17] A. de Roy, J. P. Besse, *Solid State Ionics* **1991**, *46*, 95.

[18] K. Lee, J.-H. Nam, J. H. Lee, Y. Lee, S. M. Cho, C. H. Jung, H. G. Choi, Y.-Y. Chang, Y.-U. Kwon, J.-D. Nam, *Electrochem. Commun.* **2005**, *7*, 113.

[19] Y. Bao, L. Cong, Z.-M Huang, Z. Weng, *J. Mater. Sci.* **2008**, *43*, 390.

[20] Y. Furukawa, K. Tadanaga, A. Hayashi, M. Tatsumisago, *Solid State Ionics* **2010**, doi:10.1016/j.ssi.2010.05.032.

[21] N. Iyi, K. Fujita, K. Okamoto, T. Sasaki, *Appl. Clay Sci.* **2007**, *35*, 218.

[22] W. Yang, Y Kim, P. K. T. Liu, M. Sahimi, T. T. Tsotsis, *Chem. Eng. Sci.* **2002**, *57*, 2945.

[23] Y. S. Li, T. S. Zhao, Z. X. Lian, *J. Power Sources* **2009**, *187*, 387.

[24] V. Bambagioni, C. Bianchini, A. Marchionni, J. Filippi, F. Vizza, J. Teddy, P. Serp, M. Zhiani, *J. Power Sources* **2009**. *190*, 241.