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Anion Conduction in Solid Electrolytes Probed by Water Transport Measurement

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The application of inorganic materials as electrolyte of alkaline fuel cell is an important task to achieve noble-metal-free and high-temperature-resistant fuel cells. In the present study, water transport during ion conduction through solid electrolyte was measured to seek inorganic materials with anion conduction. We discovered the anion conduction in layered oxide NaCo_2O_4 . Although LiCoO_2 has the similar layered structure to NaCo_2O_4 , this oxide showed cation conduction.

Introduction

Fuel cells have been investigated extensively as an alternative power source for solving energy/environmental problem. By using fuel cells, it is possible to extract electric energy with high efficiency through the production of H_2O from H_2 and O_2 with clean exhaust gas. Despite over decades of intensive research, the high costs of fuel cells still inhibits commercialization. Alkaline fuel cells (AFCs) appear to be the most promising technology on a cost basis. The reasons for the increasing interest in such fuel cells are as follow.¹ First, it is possible to use non-precious metals as cathode catalyst because the electro kinetics of oxygen reduction reaction at the cathode in an alkaline media is much higher than that in an acid media. Second, Ni, Co and some transition metals can be used as anode catalyst since the operation condition is alkaline. Recently some researchers reported AFC using anion exchange membrane as electrolyte,²⁻⁴ which is easily-handled because the electrolyte is solid. However, in this case, it is difficult to operate at higher temperatures than 60°C . Therefore, inorganic electrolytes with anion conduction are strongly required to achieve noble-metal free and high-temperature-resistant AFC.

The aim of this study is to determine the charge carrier in inorganic solid to seek suitable electrolyte for AFC. The charge carriers in layered oxide NaCo_2O_4 and LiCoO_2 are reported.

Experimental

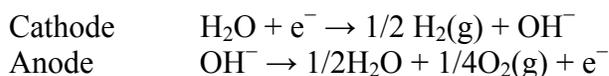
Preparation of NaCo_2O_4 and LiCoO_2

NaCo_2O_4 was prepared by dry-up method. CH_3COONa and $(\text{CH}_3\text{COO})_2\text{Co}\cdot 4\text{H}_2\text{O}$ (purchased from Wako Pure Chemical Industry, Ltd.) were dissolved in distilled water. This solution was dried with stirring, and kept in an oven overnight at 80°C . The dried powders were calcined at 750°C for 5 h. This calcined sample was ground to a fine powder and pressed into pellet. The pellets were calcined at 790°C for 3 h and crushed. The NaCo_2O_4 powders were obtained and used to make a NaCo_2O_4 disk for the test of determination of a charge carrier. The NaCo_2O_4 powder was pressed into a disk with 20 mm diameter and 1 mm thickness. The disk was sintered at 900°C for 32 h.

LiCoO₂ was prepared by a standard solid state reaction method from stoichiometric amounts of commercial oxide and carbonate. Li₂CO₃ and Co₃O₄ (purchased from Wako Pure Chemical Industry, Ltd.) powders were milled by mortar and pestle for 10 h. The milled powders were then calcined at 900°C for 3 h. The LiCoO₂ powders were obtained and used to make a LiCoO₂ disk for the test of determination of charge carrier. The LiCoO₂ powder was pressed into a disk with 20 mm diameter and 1 mm thickness. The disk was sintered at 900°C for 10 h.

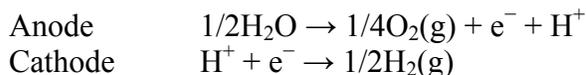
Water transport measurement apparatus

An apparatus was made to measure the transport of water through membranes during the electrolysis of an aqueous solution of an electrolyte (H₂SO₄ with pH 2.1 and 5.1, and NaOH with pH 11.9) across membranes.⁵ A Nafion NRE-212 membrane, an AEM (provided by Tokuyama Co. Ltd.), NaCo₂O₄ and LiCoO₂ were immersed in the aqueous solution, as shown in Fig. 1. An electric current was passed between two Pt electrodes through the membrane, and changes in the volumes of the aqueous solution at the anode and cathode were measured by capillary tubes. During OH⁻ conduction, the following reactions occurred



When a potential was applied across the membrane, the water moved with the anions from the cathode to the anode. Each OH⁻ ion was accompanied by n molecules of H₂O. The ratio of the decrease in H₂O at the cathode to the increase in H₂O at the anode was $(1 + n)/(1 + n)$ (≈ 1 when $n \gg 1$).

During H⁺ conduction, the following reactions occurred



When a potential was applied across the membrane, the water moved with the cations from the anode to the cathode. Each H⁺ ion was accompanied by n molecules of H₂O. The ratio of the decrease in H₂O at the anode to the increase in H₂O at the cathode was $(1/2 + n)/n$ (≈ 1 when $n \gg 1$). Thus, we could determine the number of water molecules n per conduction of one ion in membranes by observing the changes in the volumes of the aqueous solutions on both sides of the cell.

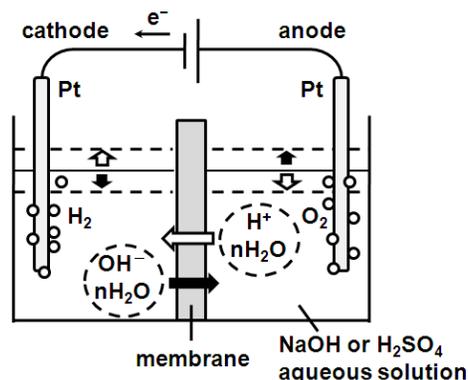


Figure 1. Principle of measurements of water-transport numbers.

Results and Discussion

XRD patterns of prepared samples are shown in Fig.2. Because there were no diffraction peaks attributed to impurity, NaCo_2O_4 and LiCoO_2 were obtained.

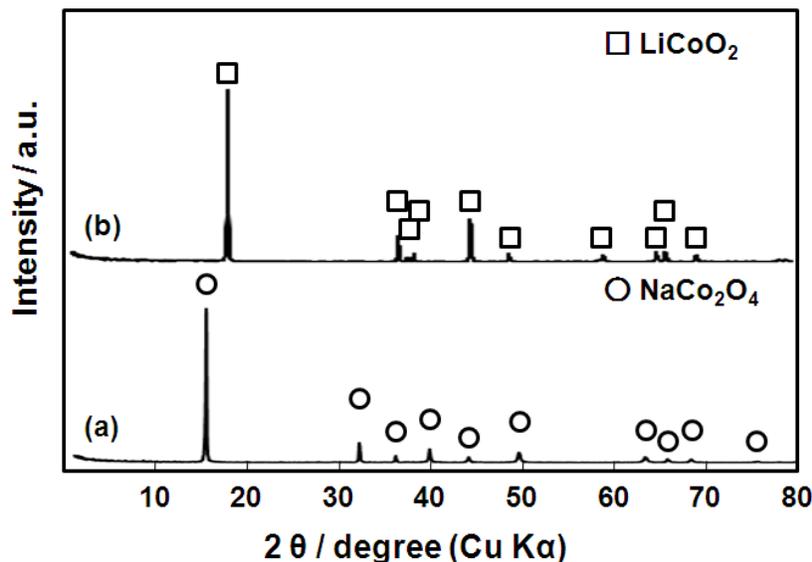


Figure 2. XRD patterns of (a) NaCo_2O_4 and (b) LiCoO_2 .

Figure 3 shows the results of water transport measurements using Al_2O_3 . In NaOH , the amount of water increased at the cathode and decreased at the anode. This result indicates that the charge carrier is cation in Al_2O_3 under alkaline conduction. At the same time, in H_2SO_4 , the amount of water increased at the anode and decreased at the cathode. This result indicates that the charge carrier is anion in Al_2O_3 under acidic conduction. Generally, when pH value is lower than isoelectric point, the charge carrier tends to be cation because the surface is negatively charged. In contrast, when pH value is higher than isoelectric point, the charge carrier tends to be anion because the surface is positively charged. The isoelectric point of Al_2O_3 is 7.0 ~ 9.0. Thus the results for Al_2O_3 are reasonable.

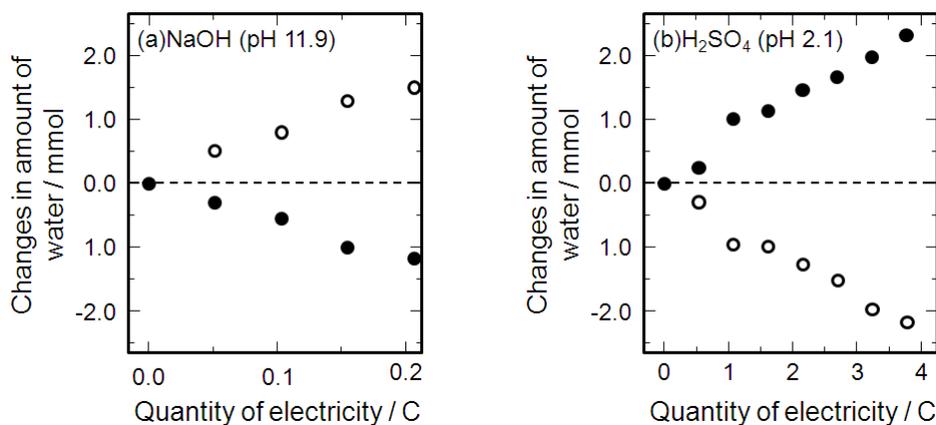


Figure 3. Changes in amount of water at the anode and cathode sides during electrolysis and electro-osmosis through Al_2O_3 . (a) Results with NaOH at pH 11.9. (b) Results with H_2SO_4 at pH 2.1. Open and closed circles are results at the cathode and the anode, respectively.

Table I shows the charge carrier in various solid electrolytes under alkaline and acidic conditions. For Nafion, the charge carrier is always cation, while for AEM, the charge carrier is always anion in both solutions. Therefore, Nafion and AEM have been used as fuel cell electrolytes.

In the case of NaCo_2O_4 , the charge carrier is anion under alkaline condition. Furthermore, n of water molecule is smaller than organic membrane. NaCo_2O_4 is expected to apply for AFC electrolyte as a new type electrolyte. In the case of LiCoO_2 , however, the charge carrier is cation even though LiCoO_2 has a similar layered structure to NaCo_2O_4 . It is suggested that the Co valence was changed by substituting Na with Li, resulting in the change in conductor. The difference of the charge carriers between these two layered oxides will be studied in the future.

TABLE I. Charge carriers in various solids under alkaline and acidic conditions.

	Charge carrier	
	Alkaline condition	Acidic Condition
Nafion	cation	H^+
AEM	OH^-	anion
NaCo_2O_4	OH^-	anion
LiCoO_2	cation	cation

Conclusions

Water transport during ion conduction in the membranes was measured to determine the charge carrier and to seek suitable electrolytes for AFC. It was revealed that the anion conduction occurred in NaCo_2O_4 even under alkaline condition. We thought that this oxide could be used for AFC electrolyte.

Acknowledgments

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