# Selective Sensing of Multi-Inorganic Ions using Ion Exchange Fiber Film

S. Hotta<sup>1</sup>, K. Miyano<sup>1</sup>, H. Aoki<sup>1</sup>, K. Kumeta<sup>2</sup>, Y. Hata<sup>2</sup>, M. Konishi<sup>2</sup>, C. Kimura<sup>1</sup> and T. Sugino<sup>1</sup>

<sup>1</sup>Department of Electrical Electronic and Information Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan Phone: +81-6-6877-5111, ext. 7699 E-mail: aoki@steem.eei.eng.osaka-u.ac.jp

<sup>2</sup> Nitivy Co., 1-2, 3-chome Kyobashi, Chuo-ku, Tokyo 104-0031, Japan

# Abstract

We have first attempted an ions sensing using an ion exchange fiber film and succeeded in selective detecting multi-inorganic ions simultaneously by using this new fiber film. The film type can easily achieve multi-layers stack and integration into the sensing devices. There is a high potentiality that the film is applicable to a high performance device for biological sensing.

# Introduction

In recent years, environmental pollution and health control problems have been focused. A simple and inexpensive sensor with rapid response has been required for monitoring our health conditions at the individual level. We have reported an ion rapid sensing using the porous ion exchanger [1]. Selective detecting a specific ion in multi-inorganic ions at a time is one of issues for conventional sensors.

In this study, we have attempted a selective sensing with a rapid response and simple structure by using an ion exchange fiber film. The fiber film type can easily achieve multi-layers stack and integration into the sensing devices. We detect inorganic ions by the impedance change of the exchange film. This paper reports electrical ion characteristics of the ion exchange fiber films adsorbed multi-inorganic ions.

#### Experimental

The ion exchange fiber film is formed using polyvinyl alcohol with conducting property. Ion-exchange functional groups such as sulfonic acid groups for cation exchanger or trimethylammonium groups for anion exchanger, are located on fiber at intervals of about 1nm as shown in Fig. 1. The impedance of the ion exchange film is increased by ion trapping, because proton hopping conduction on the functional groups is prevented due to ion adsorption on the functional groups. The cation (anion) exchange film was initialized to  $H^+$  (OH<sup>-</sup>) substitution by dipping in 1mol/ml HCl (NaOH) followed by rinsing with deionized water.

We measured the impedance of the fiber film with 300µm thickness after dipping in a solution containing inorganic ions. The film impedance was measured at 10kHz. NaCl solution and CaCl<sub>2</sub> solution were used as a typical inorganic sample, and set the amount of 10ml through all experiments.

# **Results and discussion**

Fig.2 shows the frequency dependence of impedance for each of adsorbed ions  $(H^+, Na^+, Ca^{2+})$ . The impedance of the cation exchange film drastically increases according to H<Na<Ca. The difference of the impedance by ion types is attributed to ion selectivity. The adsorption force of ions depends on the valence of ion, the ion radius and hydrated radius as shown in Fig.3. The Ca<sup>2+</sup> ions with strong adsorption exhibited large impedance.

We measured the dependence of impedance on Ca<sup>2+</sup> concentration. The impedance increases with increasing concentration as shown in Fig. 4. It was found that Ca<sup>2+</sup> ion with a concentration as low as  $10^{-6}$  mol/l can be detected.

We have attempted the impedance of the solution (NaCl, CaCl<sub>2</sub> :0.1mol/l) containing two type cations (Na<sup>+</sup>,  $Ca^{2+}$ ). Fig.5 shows the dependence of the impedance on the ratio of  $Ca^{2+}/(Na^++Ca^{2+})$ . The impedance increased with increasing ratio of  $Ca^{2+}$ . It is supposed that a kind of ion in the solution containing two kinds of cation can be detected by using calibration curve method.

We have also investigated detecting anion and cation simultaneously by using double layer film. The cation exchange film as the first layer was stacked on the anion exchange film as shown in Fig.6. As an example, CaCl<sub>2</sub> solutions of various concentration were prepared. Fig.7 and Fig.8 show the dependences of the impedance change on  $Ca^{2+}$  and  $Cl^{-}$  concentration, respectively.  $Ca^{2+}$  ions were adsorbed on the cation exchange film and Cl on the anion exchange film. On both films, the impedance depends on the concentration of the solutions. It was found that detecting multi-inorganic ions simultaneously with a concentration as low as 10<sup>-5</sup>mol/l. In addition, it is probable that this fiber type film can achieve high sensitivity, because the type film can condense ions by pouring a low concentration solution into the film.

# Conclusion

We have succeeded in selective detecting multi-inorganic ions with a concentration as low as 10<sup>-5</sup>mol/l by a sensing device using the ion exchange fiber film. The detection level is sufficient for ion concentrations in blood and drinkable water. There is a high potentiality that the ion exchange fiber film is applicable to a high performance device for biological sensing.

# Reference

[1] H.Aoki et.al., Polymer Engineering and Science, DOI 10.1002/pen (2007).



Fig.1 SEM photograph of ion exchange fiber film and its structure.



Fig.2 |Z| of the cation exchanger adsorbed each ions  $(H^{\scriptscriptstyle +},Na^{\scriptscriptstyle +},Ca^{2\scriptscriptstyle +})$ 



Fig.3 The image of hydrated radius for Na<sup>+</sup> and Ca<sup>2+</sup>.



Fig.4 |Z| change dependence of the cation exchange film on Ca<sup>2+</sup> concentration



Fig.5 |Z| change of the cation exchange film on ratio of  $Ca^{2+}/\left(Na^{+}{+}Ca^{2+}\right)$  in the mix solution.



Fig.6 Simultaneous detecting by using double layer film anion and cation.



Fig.7 |Z| change of the anion exchanger on  $Cl^{-}$  concentration in the double layer film.



Fig.8 |Z| change of the cation exchanger on  $Ca^{2+}$  concentration in the double layer film.