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Ion Exchange Properties of NASICON-type Ceramics—Application to Ion Selective Electrodes

F. Mauvy and E. Siebert*

Laboratoire d'Electrochimie et de Physicochimie des Matériaux et des Interfaces (Laboratory INPG, associated to CNRS UMR 5630, and to University J.Fourier—Grenoble), ENSEEG, 1130 rue de la piscine, BP 75-38402 Saint Martin d'Hères cedex, France

Abstract

The ion-exchange properties of NASICON type ceramics of composition $Na_3Zr_2Si_2PO_{12}$ were investigated in aqueous solutions of NaCl, LiCl and KCl. The solution analysis shows that the $[Zr_2Si_2PO_{12}]$ framework strongly prefers Na^+ ion relative to K^+ and Li^+. The exchange current density of the alkali-cations at the NASICON/solution interface determined by impedance measurements varies in the order $Na^+ > Li^+ > K^+$. These results agree well with the selectivity coefficients of Na^+ ion selective electrodes based on NASICON. The interference process to alkali-cations in the NASICON based electrode was shown to result from an ionic exchange. The selectivity was suggested to be governed by the mobility of the cation inside the NASICON framework. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

(NASICON) Na Super Ionic CONductor is the acronym of the solid solution of composition $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$. It was first synthesized by Hong in 1976.[1] This compound has a rigid anion framework built of ZrO_6 octahedra and $(Si,P)O_4$ tetrahedra. It exhibits high Na^+ conductivity for compositions for which $1{\cdot}8 < x < 2{\cdot}2$ ($\sigma = 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at room temperature, for the $x = 2$ composition). The NASICON ceramic has been proposed as the sensitive membrane of Na^+ ion selective electrode (ISE).[2] The main advantage with respect to the classical glass electrodes is the better selectivity which was proposed to result from the calibration of conductive sites in the NASICON structure.[3]

The aim of the present work is to further investigate the selectivity process in the NASICON ceramic. The ionic exchange properties of NASICON compound in aqueous solution have been investigated by X-ray diffraction and solution analysis. Furthermore, the ion exchange current density of alkali-cation at the NASICON/solution interface has been measured by impedance spectroscopy. Besides those measurements, the selectivity coefficients of NASICON based Na^+ ISE have been determined to look for any correlation.

2 Experimental

2.1 Materials

The $Na_3Zr_2Si_2PO_{12}$ compound was obtained by the sol/gel process as described in Ref 4. Pellets of high density were obtained by isostatic pressing and sintering under air, at 1000°C. Their density was of the order of 90% of the theoretical density. The purity of the sample and crystallographic structure were checked by X-ray diffraction. Pure single phase NASICON and NASICON containing a small amount of ZrO_2 were tested. This ceramic crystallised in a monoclinic (or pseudo-rhombohedral) structure.

2.2 Ionic exchange

A weighed amount of NASICON powder was suspended in LiCl and KCl 0.1 M aqueous solution, during four days, at room temperature. After exchange, the solution was separated from the powder and analysed by ICP-AES method. The Na concentration in solution was determined with a precision of 5%. The experiments were performed in the Compagny Science & Surface S.A., France.

The residual NASICON powder was dried and analysed by X-ray diffraction to check the stability

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*To whom correspondence should be addressed. Fax: +33-476-826-670; e-mail: elisabeth.siebert@lepmi.inpg.fr of the NASICON framework. All the exchanged powders were found to exhibit the NASICON-type crystallographic structure.[5]

2.3 Impedance measurements—determination of i_0

The exchange current density of the alkali-cations (Na^+, Li^+ and K^+) at the NASICON/aqueous solution interface was measured by four electrode impedance measurements as depicted elsewhere.[6] Impedance measurements were performed at room temperature, in aqueous solutions of NaCl, LiCl and KCl. $BaCl_2$ 0·1 M was used as the supporting electrolyte. They were carried out in the frequency range 65 kHz–0·1 Hz, with an applied ac signal of 20 mV. A Solartron 1250 Frequency Response Analyser coupled to a 1186 Electrochemical Interface (Schlumberger) was used.

Figure 1 shows typical impedance diagram of the NASICON pellet in contact with a 0·1 M NaCl, LiCl or KCL solution, respectively. These diagrams have been analysed in detail in Ref. 7.

The exchange current densities i_0 were deduced from the semi-circle in the frequency range 10^4–10^1 Hz, according to the following relationship:

$$i_0 = \frac{RT}{FS} \times \frac{1}{R_{\mathrm{INT}}} \tag{1}$$

where R_{INT} is the interfacial resistance deduced from the intercept of the semi-circle with the real axis and S is the NASICON/solution interface surface area.

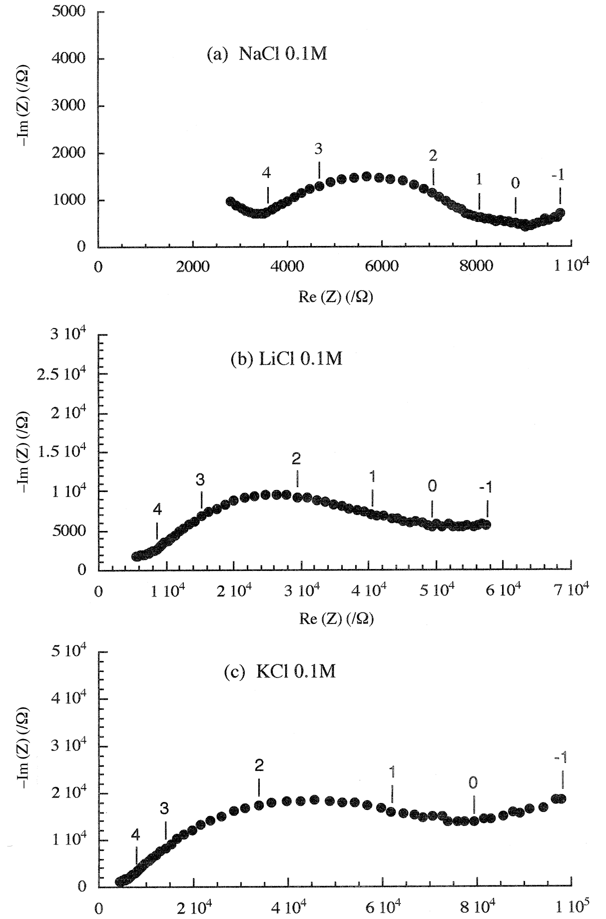

Fig. 1. Impedance diagrams in Nyquist plan of the NASICON membrane in contact with 0·1 M (a) NaCl, (b) LiCl, and (c) KCL, solutions. The numbers on the diagrams represent the logarithms of the frequency.

2.4 Potentiometric measurements—determination of $K^{POT}_{Na,I}$

The selectivity coefficient of the Na^+ ISE based on NASICON was determined by potentiometric measurements as proposed by I.U.P.A.C.[8] The following electrochemical chain:

Saturated Calomel Electrode (SCE)/Solution/NASICON pellet/NaCl 0·1 M/AgCl-Ag was used. The voltage was measured between the SCE and silver wire. Aqueous solutions were prepared with $BaCl_2$ 0.1 M as the supporting electrolyte. Figure 2 gives a typical example of a calibration curve for Na^+, Li^+ and K^+ ions. The potentiometric selectivity coefficients, $K^{\mathrm{POT}}_{\mathrm{Na,I}}$, were determined by identification of these calibration curves with the Nicholkii–Eisenmann relationship taking into account the detection limit D.L. according to the following equation:

$$E = E^o + \frac{RT}{F}\ln\left(a_{\mathrm{Na}} + K^{\mathrm{POT}}_{\mathrm{Na,I}} \times a_{\mathrm{I}} + \mathrm{D.L.}\right) \tag{2}$$

where a_{Na} is the sodium activity and a_{I} represents the activity of the I^+ interfering cations in the analysed solution. E^o is a constant depending on the reference systems. R, T and F have their usual meanings.

3 Results and Discussion

The ion exchange fractions determined from solution analysis are assembled in Table 1. The ionic exchange current densities measured in 1 M NaCl, LiCl and KCl solutions are also reported as well as

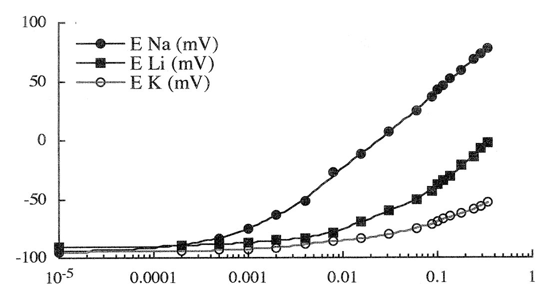

Fig. 2. Potentiometric response curves of $Na_3Zr_2Si_2PO_{12}$-membrane to Na^+, Li^+ and K^+ ions measured in $BaCl_2$ 0·1 M as supporting electrolyte.

Table 1. Potentiometric selectivity coefficient $K^{\mathrm{POT}}_{\mathrm{Na,I}}$, standard ion exchange current density i_0 measured at concentration equal to 1 M and exchange fraction for the Na^+, Li^+ and K^+ ions

Cation	$K^{\mathrm{POT}}_{\mathrm{Na,I}}$	i_0 *(A cm^{-2})*	*Exchange fraction (%)*
Na^+	—	$4{\cdot}410^{-5}$	—
Li^+	0·06	$6{\cdot}4\ 10^{-6}$	59
K^+	0·01	$3{\cdot}0\ 10^{-6}$	66

the potentiomettic selectivity coefficients. The NASICON of composition $\mathrm{Na_3Zr_2Si_2PO_{12}}$ exchanges Li^+ and K^+. When it is contacted with solutions containing LiCl or KCl, a solid-solution $\mathrm{Na}_{3\text{-}x}\mathrm{I}_x\mathrm{Zr_2Si_2PO_{12}}$ is formed. The exchange is only partial indicating that the $(\mathrm{Zr_2Si_2PO_{12}})$ framework strongly prefers the Na^+ ions. In agreement with this result, the best selectivity is obtained for the Na^+ ions as well as the highest exchange current density. Comparison between the different cations shows that the ionic exchange currents at the NASICON/water interface are in the order: $i_0(\mathrm{Na}) > i_0(\mathrm{Li}) > i_0(\mathrm{K})$. In parallel, the values of the potentiometric selectivity coefficients show that the selectivity varies in the order Na > Li > K. It appears that the selectivity properties correlate with the ionic exchange current densities. The higher the exchange current density is, the higher the selectivity coefficient. Moreover, a high apparent ion exchange current density of the membrane corresponds to behaviour as a good nernstian sensor.

The interference process to alkali-cations in NASICON based ISE can therefore be proposed to result from an ionic exchange. Eisenman's model describes the potentiometric selectivity of ISE based on ionic exchange equilibrium.[9] The potentiometric selectivity coefficient can be expressed as a function of the mobilities of the primary U_{Na}, and interfering u_{I} cations inside the membrane and the exchange equilibrium constant K_{exch} according to the following equation:

$$K^{\mathrm{POT}}_{\mathrm{Na,I}} = \frac{u_{\mathrm{I}}}{u_{\mathrm{Na}}} \times K_{\mathrm{exch}} \tag{3}$$

The results of Table 1 show that the exchange constant for Li^+ and K^+ are almost the same while the selectivity coefficients are different. It allows us to suggest that the difference of selectivity comes from the difference of mobility of the cations inside the membrane, in the order $\mathrm{Na}+ > \mathrm{Li}^+ > \mathrm{K}^+$. The rate of exchange of the alkali-cations at the interface seems also to vary in the same way as the mobility of the cations in the structure.

4 Conclusion

The interference process to alkali-cations in NASICON based ISE was shown to result from an ionic exchange between the NASICON framework and the solution. The selectivity was rather fixed by the mobility of the cations inside the NASICON and varied in the same way as the cations exchange current density.

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