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ELECTROCHEMICAL MATERIALS SCIENCE

EPMA STUDY OF "NASICON" SOLID ELECTROLYTE

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Electron probe micro analysis was performed on "NASICON" solid electrolyte. The mobile sodium ions move towards the electron beam and get converted into atoms. Results are presented.

Key Words: NASICON, solid electrolyte, ion mobility

INTRODUCTION

Electron probe micro analysis (EPMA) is usually employed for elemental analysis. Recently [1] this technique was employed as charge supply electrode to the fast ion conductors, viz. beta alumina and NASICON. These ion conductors have mobile cations. When they are subjected to electron bombardment, electrons are trapped by mobile cations and transformed into atoms [2]. Here the electron beam itself serves as cathode. Sodium X-ray counts of polycrystalline beta alumina were reported [3] to be increased gradually during the electron bombardment. NASICON solid electrolyte was also subjected to electron bombardment. EPMA curve was taken and sodium deposition on NASICON was photographed. Results are presented in this short communication.

EXPERIMENTAL

NASICON powder was synthesized [4] from calculated quantities of AR Grade Na_2CO_3, ZrO_2, SiO_2 and $NH_4H_2PO_4$ to achieve a final composition corresponding to Na_3Zr_2 Si_2 PO_{12}. The mixture was ball milled as acetone slurry for 16 hours. The product was slowly dried and decomposed at 170°C for 16 hours. Resulting powder was then calcined at 900°C for 4 hours. The powder was then ground in agate mortar for uniformity and calcined again at 1100°C for 4 hours. The fully decomposed powder was then vibromilled so as to obtain the particle size around 1 to 3 um. Pellets of suitable dimension could be pressed out from this powder in a floating steel die set-up.

Sodium (K- α) X-ray counts were collected throughout the electron bombardment time on NASICON using EPMA technique, available as accessory in scanning electron microscope instrument (JEOL JSM 35 CF). The electron beam was fixed coresponding to sodium wavelength to a selected point on the surface of the pellet and also scanned over the area of the pellet. Regions of sodium accumulation and deposition were picked out and phtographed. In this case, there was no need to have a conductive coating on the pellet. Electron probe itself is used as cathode and the mobile ions are discharged at this electrode.

RESULTS

Sodium accumulation and deposition

In Nasicon sintered compact, three dimension conducting grains are randomly oriented. Fig.1 reveals the deposition of white droplets of sodium on NASICON compact.

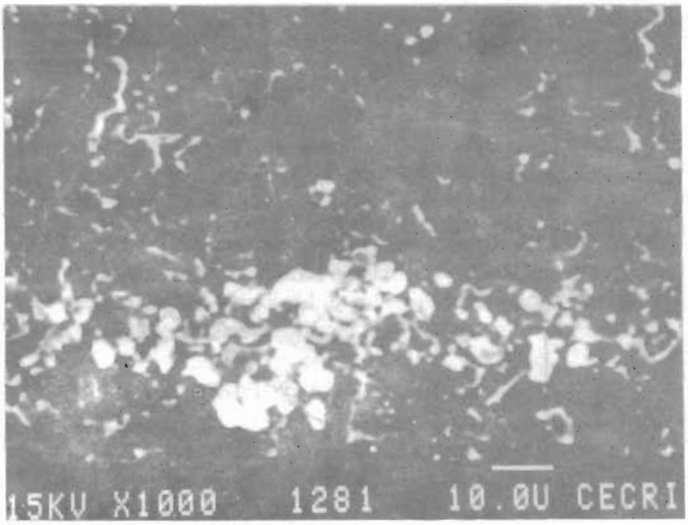

Fig.1: Deposition of white droplets of sodium on NASICON Compact

Fig.2 is a typical EPMA ion mobility curve and it is the result of the interactions between the injected electrons (beam current 1.96 μA) form EPMA and the fast ionic solid electrolyte, viz. NASICON. Electrons of high energies will excite X-ray photons which are responsible for elemental analysis and electrons with lowered energy will neutralise the cation carrier [2].

Fig.3 depicts the counts of the characteristic X-ray per second (CPS) versus time.

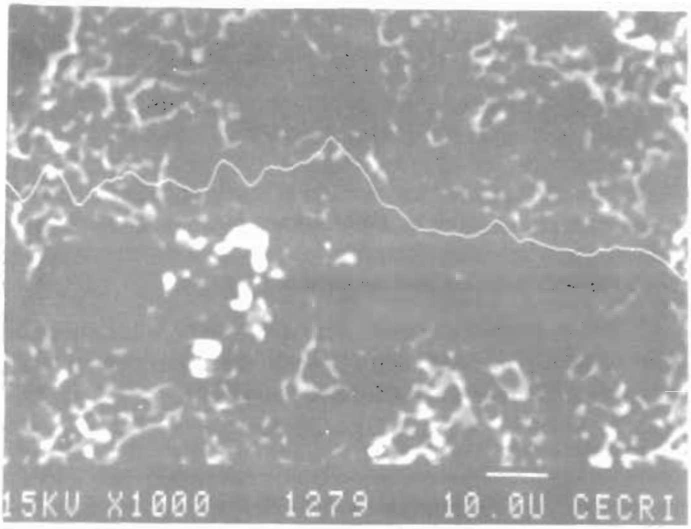

Fig.2 EPMA ion mobility curve result of interactions between injected electrons and NASICON solid electrolyte

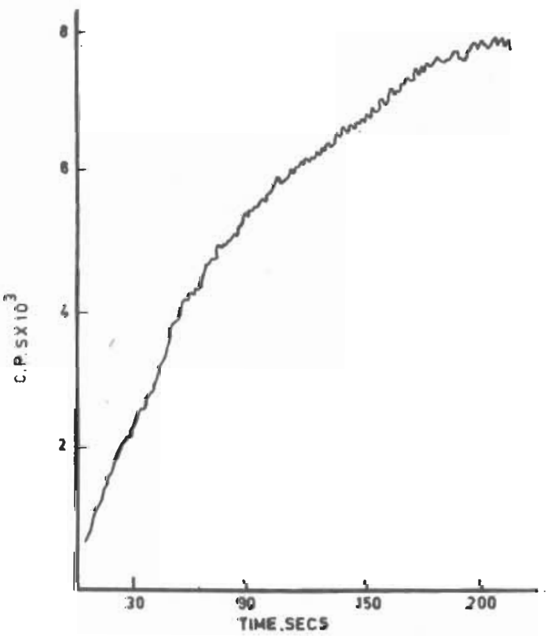

Fig.3: EPMA curve of sodium super ion conductor NASICON polycrystal; Experimental conditions Voltage = 15 kV, beam current = 15 nA and beam diameter = 10 μA

This graph can be used to evaluate the quantities of the ionic and atomic deposits. The expression for time dependence of sodium accumulation dealt in [1] is given by

$$Q = a \left[1 - \exp(-bt) \right] + Q_0 \exp(-bt)$$

where $a = m_0 / k_2$

$b = k_1 k_2 \sigma E/n$

Q = quantity of deposits
t = time
E = strength of the electrical field
n = concentration of major carrier
= ionic conductivity $\quad m_0$ = initial concentration
k_1 = constant characteristic of the experimental conditions
k_2 = another constant $\quad Q_0$ = the value of Q at t = O

At infinite time, saturation limit is reached and this corresponds to the value of a. Using the above expressions and from Fig.3 the values of a, b and Q_0 are calculated and given below:

a = 94275 $\quad$ b = 0.0374 $\quad$ Q_0 = 14030

From the standard sample of sodium carbonate pellet, counts per second were obtained and % of sodium was evaluated and tabulated (Table I).

Table I : Percentage of sodium in NASICON sample evaluated from EPMA study

Time in secs	Percentage of Na
30	16.5
60	39.0
90	60.0
120	70.0
150	81.0
180	89.0
200	99.5

From the Table it is seen that accumulation tends to saturation at 200 sec which is evident from the Fig.3 also.

CONCLUSION

ICON solid electrolyte was subjected to electron bombardment and typical ion mobility curve was presented. Sodium accumulation with time was calculated from the standard sample and it agrees well with the experimental ion mobility curve.

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