Mat. Res. Bull., Vol. 21, pp. 357-363, 1986. Printed in the USA.
0025-5408/86 $3.00 + .00 Copyright (c) 1986 Pergamon Press Ltd.

NASICON SOLID ELECTROLYTES

PART IV

CHEMICAL DURABILITY

K.D.Kreuer and U.Warhus
Max-Planck-Insitut für Festkörperforschung
Heisenbergstr.1 7000 Stuttgart 80, Germany F.R.

(Received January 3, 1986; Communicated by A. Rabenau)

ABSTRACT

The chemical durability of NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, x=0-3) versus molten sodium and sulfur at 600 K has been investigated. Degradation by molten sodium has been observed for phosphorus-containing compositions only. The pure silicate (x=3), however, appeared to be stable, because reduction of silicon demanded by thermodynamics did not occur at the given temperature for kinetic reasons. The latter composition has also been shown to have good durability against molten sulfur.

MATERIALS INDEX: NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, x=0-3)

1.INTRODUCTION

There is an extensive literature about electrical transport and structural properties of materials of the NASICON family ($Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$, x=0-3) but information about their chemical stability, which is important for the application of such materials in electrochemical cells, is still limited.

There have been static corrosion tests of NASICON ceramics in liquid sodium (1-3) and dynamic cell tests on some selected NASICON compositions (x= 2 and 2.4) in sodium/sodium and sodium/sulfur cells (3-5). All experiments indicate some corrosion of NASICON in molten sodium, although the kinetics of the reaction depended very much on the sample preparation.

Recently, the availability of thermodynamic data (6) for the NASICON solid solution system (x= 0-3) has allowed the setup of critical corrosion reactions of NASICON with sodium including their thermodynamics. The corresponding GIBBS free energies of reaction (Δ_rG) are negative for all compositions indicating thermodynamic instability of NASICON against sodium.

In this paper the predicted reactions will be inspected by different types of static corrosion tests for all NASICON compositions. In addition, the reaction of NASICON (x=3) with sulfur will be examined.

2.EXPERIMENTS AND RESULTS

2.1.Durability against molten Sodium

For the study of the direction of a chemical reaction different approaches are possible. We tried to identify NASICON degradation in the presence of molten sodium, to identify possible reaction products and to get an indication of reverse reactions.

The most straightforward experiment is simply to expose NASICON to an excess amount of sodium in a closed tube *. The sodium metal was removed by vacuum distillation before the residual powder was examined by SEM, IR-spectroscopy and X-ray powder diffraction. Thus the durability of the NASICON compositions x= 0, 0.5, 1, 2, 2.5 and 3 (for preparation see (7)) have been tested at 600 K for different times. For all compositions containing phosphorus the characteristic smell of phosphine upon opening the tube indicated the formation of moisture sensitive sodium phosphides (e.g. Na_3P) and therefore a degradation of NASICON. The reaction, however, depended very much on the individual sample. For a fine powder (grain size ca. 1µm) the reaction was complete after several minutes for phosphate rich compositions (x= 0, 0.5, 1) and several days for silicate rich samples (x= 2, 2.5). For the first, X-ray diffraction revealed the black reaction products to be amorphous, for the latter only NASICON (x=3) could be identified as a reaction product. Especially for x= 2.5 this NASICON phase was well crystallized. For ceramics of high density (93-97%) and high silicate content (x=2), however, no degradation could be observed after one week by SEM and no other phase beside NASICON could be identified in the in the IR-spectra and the X-ray diffraction pattern.

This was also true for the pure silicate (x=3); therefore more sensitive experiments were carried out with this composition.

A submicron NASICON powder prepared by a sol/gel technique (8) was exposed to sodium for one week (T=600K). Besides a change in color, which turned from white to dark brown, no alteration was observed. The powder could easily be dissolved in diluted HF and no residue, in particular no reduced silicon could be identified.

In addition the dried sol/gel precursor was heated in the presence of sodium in a dry box, and for temperatures above about 1000 K the formation of NASICON and Na_2SiO_3 has been observed by X-ray diffraction.

In order to exclude the possibility that a degradation reaction occurs at the NASICON surface only, an electrochemical cell was designed. It takes advantage of a slight electronic conductance of NASICON (x=3) in a reducing environment (the electronic properties of the ceramics very much depend on grain boundary properties (8)) on account of which NASICON can be used as an electrode material. It was first equilibrated with molten sodium and the black pellet was then used in a cell of the type:

(+) Pt / NASICON / Na-β''alumina / Na / Pt (-) (T= 600 K)

The initial cell voltage was of the order of some 10 mV. Sodium was coulometrically titrated into the NASICON in an amount which corresponded to 1% of the total sodium content of the pellet. The resulting potential difference

---

* Quartz glass and niobium tubes have been used. For all experiments with the pure silicate (x=3) it should be noted that there is poor wetting of NASICON by molten sodium at 600 K. Therefore all all reactants were initially heated to about 1000 K to ensure good contact between NASICON and sodium.

was close to 0 mV due to the excess sodium in the NASICON electrode. If a reaction of this sodium and NASICON occurred consuming the sodium completely and leading to reaction products with a lower sodium activity, an increase of the potential difference would be expected with time. This, however was not the case, the cell-voltage remaining close to 0 mV for more than one week.

The following tests especially concentrate on the degradation reaction of NASICON (x=3) which has been shown to be the reaction with the greatest affinity (6):

$$Na_4Zr_2Si_3O_{12} + 6\ Na \rightarrow 2\ Na_2ZrO_3 + 1.5\ Na_4SiO_4 + 1.5\ Si\ (\Delta_rG_{600K} = -130 kJmol^{-1})$$

The first test was used to identify silicon as a reaction product. A hot-pressed and polished NASICON pellet was exposed to liquid sodium (600 K, one week). The adherent sodium then was removed by distillation in vacuum at a temperature above the stability regime of any sodium silicide (693 K,420 °C) (9). The IR-reflection spectrum of the pellet surface provided no indication of formation of silicon.

Secondly, the reverse reaction has been tested. Na_2ZrO_3, Na_4SiO_4 (prepared following (10)) and silicon were intimately mixed according to the stoichiometry of the above reaction and pressed into a pellet. The pellet was embedded in silicon powder to prevent oxidation and annealed in a furnace. After one night at 1223 K (950 °C), Na_2ZrSiO_5, ZrO_2 and NASICON could be detected by X-ray diffraction; after another night at 1273 K (1000 °C) the pellet consisted of NASICON only and its color had turned to white (the silicon encapsulation was still grey). Unfortunately the reaction kinetics prevents equilibration at lower temperatures, but for temperatures above 1223 K (950 °C) the experiment provides evidence for the reverse reaction.

2.2. Durability against molten sulfur

The durability of only NASICON (x=3) against molten sulfur (T= 600 K) has been tested. A possible reaction is:

$$Na_4Zr_2Si_3O_{12} + 4\ S \rightarrow 3/4\ Na_2S_5 + 1/4\ Na_2SO_4 + Na_2ZrSi_2O_7 + ZrSiO_4$$

The formation of Na_2SO_4 has already been shown during the degradation of sodium silicate glasses (11). With the thermodynamic data listed in table 1 its GIBBS free energy of reaction is slightly negative with $\Delta_rG_{300K} = -49.1$ kJ mol^{-1} and $\Delta_rG_{600K} = -74.2$ $kJmol^{-1}$. This, however, could not be confirmed by the experimental result. NASICON powder has been sealed into an evacuated quartz tube together with excess sulfur and kept at 600 K for one week. No reaction has been observed by SEM and X-ray diffraction; only NASICON (x=3) and monoclinic sulfur could be identified.

3. DISCUSSION

The chemical durability of NASICON against sodium will be discussed with the help of fig.1. It shows the GIBBS free energy of the specified reactions as a function of the NASICON composition. Reaction 1 and 2 are thought to represent the degradation of NASICON against sodium (6). Indeed, for all NASICON compositions containing phosphorus (x<3) degradation is observed, but with the exception of phosphines there is no indication of any of the claimed

TABLE 1
GIBBS free energy of formation ($\Delta_f G$) for the given compounds at 300 and 600 K. The data used for the calculation of the GIBBS free energy of the reactions ($\Delta_r G$) shown in fig.1 are indicated by *.

phase	$\Delta_f G^o_{300,K}$ [kJ mol^{-1}]	$\Delta_f G^o_{600,K}$ [kJ mol^{-1}]	method of determination	ref.
NASICON				
x=0	-4560.0	-4233.3	EMF, DSC, ADC	(6,12)
x=3	-5937.0 *	-5574.0 *	EMF, DSC, ADC	(6,12)
	-6016.0	-5652.5	HCl-calorimetry ($\Delta_f H$)	(13)
			EMF,DSC,ADC (S)	(6,12)
Na_2ZrO_3	-1570.8 *	-1472.1 *	EMF	(14)
	-1589.8	-1489.6	DSC,HCl-calorimetry	(15)
Na_4SiO_4	-1952.3	-1812.3		(16)
	-1975.3 *	-1836.1 *	estimated	(17)
Na_2SiO_3	-1467.4	-1368.7		(18)
Na_2O	-376.1	-333.6		(19)
ZrO_2	-1012.79	-984.92		(19)
Na_2ZrSiO_5	-2508.2	-2354.3	HCl-calorimetry ($\Delta_f H$)	(20)
			cp (S)	(21)
Na_3P	-85	-66.6	($\Delta_f H$)	(18)
			S estimated	(12)
Na_2S_5	≈450	-400.83	EMF	(22)
Na_2SO_4	-1269.35	-1144.71		(18)
$Na_2ZrSi_2O_7$	-3412.4	-3258.0	HCl-calorimetry ($\Delta_f H$)	(13)
			cp (S)	(12)
$ZrSiO_4$	-1918.89	-1803.38		(19)

eaction products, particularly no reduced silicon. Instead, the silicate end member (x=3) was observed as a reaction product for x≥2. This is important in two respects:

First the degradation reaction for phosphorus containing NASICON deviates from reaction 2 (fig.1).

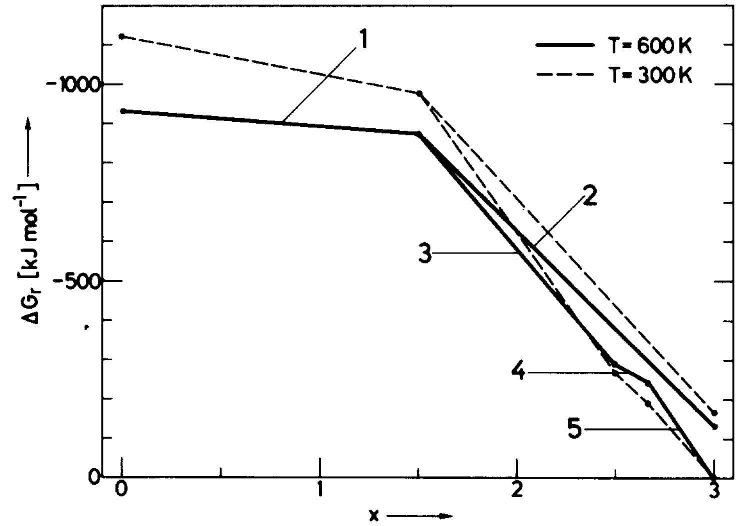
Second, during the degradation reaction the material is certainly highly reactive and the formation of NASICON (x=3) in this situation implies that under the experimental conditions (T=600 K) any NASICON (x=3) is not expected to react with sodium, which is verified by the experiments with the pure silicate.

But this does not necessarily prove the thermodynamic stability of the pure silicate against molten sodium. There is some uncertainty in the thermodynamic data (table 1), which is, however, within the range of thermodynamic instability of NASICON (x=3). If we additionally consider the instability of silicon versus sodium with respect to the formation of silicides below about 693 K (420 °C) (9) the GIBBS free energy of reaction 2 (fig.1) is expected to be even more negative (unfortunately no thermodynamic data are available for silicides)

A possible explanation for the deviation of the experiment from thermodynamics may be that breaking of the covalent Si-O bond of the SiO_4- tetrahedra involved in the reduction of silicon does not take place at the given temperature for kinetic reasons and therefore complete thermodynamic equilibrium may not be attained. One also has to keep in mind that the presence of oxygen, which can be dissolved in sodium (23,24), may have slightly reduced the sodium activity.

Similar results have been obtained for the reaction of silicate glasses with sodium. The formation of Na_2SiO_3, which is thermodynamically unstable against sodium (25), has been observed in the degradation of silicate-rich glasses (26), but reduction of silicon could not be proven unambiguously. The coloration of the reduced glasses is frequently interpreted in terms of the formation of color-centers (e.g.27) rather than by precipitation of reduced silicon. We therefore looked for possible reactions of NASICON with sodium using the program of FINGER and BURT (28) with the boundary condition that silicon is not reduced. The reactions with the lowest GIBBS free energies are denoted 3,4 and 5 in fig.1. They seem to be closer to the experimental situation than reaction 2 (fig.1). They are consistent with the observed instability of all NASICON compositions containing phosphorus and the durability of the pure silicate only. In addition reaction 5 (fig.1) agrees with the formation of NASICON (x=3) during the degradation of silicate-rich NASICON compositions.

Finally, let us consider the temperature dependence of reaction 2 (fig.1). As can be seen from the figure the GIBBS free energy of reaction at room temperature is significantly lower compared to 600 K. Following this trend we would expect a decreasing thermodynamic instability of NASICON versus sodium for temperatures above 600 K. For the pure silicate the temperature above



1: (3-x) Na_3P + 2 Na_2ZrO_3 + x Na_4SiO_4 + (6-4x) Na_2O

2: (3-x) Na_3P + 2 Na_2ZrO_3 + x Na_4SiO_4 + (x-1.5) Si

3: (3-x) Na_3P + (5-2x) Na_2ZrO_3 + (3-x) Na_4SiO_4 + (2x-3) Na_2ZrSiO_5

4: (3-x) Na_3P + (4x-10) Na_2SiO_3 + (8-3x) Na_4SiO_4 + 2 Na_2ZrSiO_5

5: (3-x) Na_3P + (6-2x) Na_2SiO_3 + (18-6x) Na_2ZrSiO_5 + (3x-8) $Na_4Zr_2Si_3O_{12}$

FIG.1
GIBBS free energy of reactions of one mole NASICON (x=0-3) with sodium at 300 and 600K calculated from the thermodynamic data listed in table 1. The reaction products are specified in the legend.

which NASICON is even thermodynamically stable against sodium is probably lower than suggested by the data given in fig.1. The identification of the reverse reaction at temperatures above about 1223 K (950 °C) suggests that $\Delta_r G$ at 600 K is less negative. Considering the experimental uncertainty of the thermodynamic data of Na_4SiO_4 (16,17) and $Na_4Zr_2Si_3O_{12}$ (6,12,13) this assumption seems to be reasonable. One has, however, to keep in mind that the evaporation of sodium may have favoured the NASICON formation.

The durability of NASICON (x=3) versus molten sulfur will be discussed briefly. For the chemical stability of glasses it is known empirically that reaction with sulfur becomes more critical as the basicity (Na_2O-content) of the material increases (probably because of the similar energies of the Na-O and Na-S bonds). NASICON (x=3) is an orthosilicate with a high Na_2O-content and, therefore, chemical instability versus sulfur can not be excluded a priori. The thermodynamic data suggest slight instability, which, however, could not be verified by the durability test. One has, however, to keep in mind that in the presence of oxygen the sulfur might react to form very stable sulfates exclusively without the formation of the far less stable sulfides as suggested by the reaction, thus leading to an additional driving force for a possible degradation.

4. SUMMARY

The chemical durability of NASICON versus sodium and sulfur at 600 K has been investigated.

The degradation reaction which has been shown to be the reaction with the greatest affinity (thermodynamic path) (6) and which involves the reduction of silicon by sodium could not be verified experimentally. Instead, reaction 3-5 (fig.1) describe the kinetic reaction path under the experimental conditions. They are in agreement with the instability of any phosphorus containing NASICON (x<3) against sodium and the durability of the pure silicate (x=3).

The latter composition has also been shown to have good durability against sulfur.

Obviously the basicity (Na_2O-content) of NASICON (x=3) is such that the GIBBS free energies of reaction with both sodium and sulfur are close to zero.

From this point of view NASICON (x=3) is of potential interest as a separator material in Na/S cells, provided that the intrinsicly low ionic conductivity can be increased, which will be the object of a forthcoming part of this series (8).

ACKNOWLEDGMENT

The authors wish to thank A.Breitschwerdt for recording the IR-spectra and J.Samson and Hj.Mattausch for reading the proofs.

REFERENCES

1. H.Schmid, L.C.DeJonghe, C.Cameron; Solid State Ionics 6, 57 (1982)

2. G.J.Tennenhouse, G.M.Crosbie; J.Am.Ceram.Soc. 67, 204 (1984)

3. R.S.Gordon, G.R.Miller, B.J.McEntire, E.D.Beck, J.R.Rasmussen; Solid State Ionics 3/4, 243 (1981)

4. Y.Tung-Sheng in: Energy and Ceramics, ed. P.Vincentini (North-Holland, Amsterdam) 1253 (1980)

5. G.Desplanches, D.Gourier, A.Wicker; Bull.Am.Ceram.Soc. 59, 377 (1980)

6. J.Maier, U.Warhus; Solid State Ionics (Proc.of the 5th Int.Conf.on SSI, Lake Tahoe, 1985) in press ; Mater.Res.Bull. in preparation

7. K.D.Kreuer, H.Kohler, U.Warhus, H.Schulz; Mater.Res.Bull. 21 (2) (1986), in press

8. K.D.Kreuer, U.Warhus; to be published

9. W.Klemm; Proc.Chem.Soc. 329 (1958)

10. K.Kautz, G.Müller, W.Schneider; Glastechn.Ber. 43, 377 (1970)

11. S.Susman, C.J.Delbecq, J.A.McMillan, M.F.Roche; Solid State Ionics 9/10, 667 (1983)

12. U.Warhus; Thesis TU Stuttgart, in preparation

13. E.V.Shibanov, V.G.Chuklantsev; Russ.J.Phys.Chem 48, 133 (1974)

14. J.Maier, U.Warhus; J.Chem.Thermodynamics, in press

15. R.P.Beyer, K.O.Bennington, R.R.Brown; J.Chem.Thermodynamics 17, 11 (1985)

16. O.P.Mcedlov-Petrosjan, V.I.Babuskin, G.M.Matveev: Thermodynamik der Silikate, VEB Verlag für Bauwesen, Berlin (1966)

17. P.J.Spencer: The Thermodynamic Properties of Silicates, Teddington, Nat.Phys.Lab., DCS Reports 21 (1973)

18. The NBS Tables of Chemical Thermodynamic Properties; Suppl. No.2 to Vol.11 of J.Phys.Chem.Ref.Data (1982)

19. R.A.Robie, B.S.Hemingway, J.R.Fisher: Thermodynamics of Minerals and related Substances, Geological Survey Bulletin 1452, Washington (1979)

20. V.G.Chukhlantsev, E.V.Shibanov; Russ.J.Phys.Chem. 42, 1224 (1968)

21. E.V.Shibanov, V.G.Chukhlantsev; Russ.J.Phys.Chem. 50, 1470 (1976)

22. N.K.Gupta, R.P.Tischer; J.Electrochem.Soc. 119, 1033 (1972)

23. H.S.Isaacs; J.Electrochem.Soc. 119, 455 (1972)

24. J.Jung, A.Reck, R.Ziegler; J.Nucl.Mater. 119, 339 (1983)

25. A.Herczog; J.Electrochem.Soc. 132, 1539 (1985)

26. C.J.Brinker, L.C.Klein; Phys.Chem.Glasses 21, 141 (1980)

27. A.J.Stryjak, P.W.McMillan; Glass Technology 20, 53 (1979)

28. L.W.Finger, D.M.Burt: Program "Reaction", Geophysical Laboratory, Washington D.C. 20008 (1972)