JOURNAL OF MATERIALS SCIENCE 17 (1982) 753–759

Wetting characteristics of sodium on ß″-alumina and on nasicon

L. VISWANATHAN, A.V. VIRKAR
Department of Materials Science and Engineering, Univeristy of Utah, Salt Lake City, Utah 84112, USA

The sessile drop technique was used to determine the wetting characteristics of liquid sodium on β''-alumina and nasicon ($Na_3Zr_2Si_2PO_{12}$). The effects of moisture and temperature were studied using the wetting experiments. A range of contact angles (from 0 to 160°) were observed. The samples exposed to moisture exhibited poor wetting. The fact that good wetting is a prerequisite for improved cell performance was demonstrated via Na $|\beta''$-alumina$|$ Na cell tests. Cells baked out in a vacuum passed in excess of 1 100 A h cm^{-2} at 4 A cm^{-2} current density without any degradation. Unbaked cells under similar conditions failed under 200 A h cm^{-2}.

1. Introduction

One of the failure modes of a sodium–sulphur (Na–S) battery [1], results from the degradation of the β''-Al_2O_3 solid electrolyte, which is a superior conductor of Na^+. The degradation occurs on the liquid sodium side of the electrolyte during the charging cycle of the cell. Pressurized sodium-filled cracks tend to propagate, causing a mechanical breakdown and/or an increase in electronic conductivity, both of which are detrimental to the life of the battery.

Many theories [2–6] have been advanced to describe this phenomenon. A theory that does not involve propagation of a sodium-filled crack has also been proposed [7]. Calculations [4, 5] of critical current density above which degradation occurs, (in which crack opening displacement is included in a natural way) indicate that degradation should not occur below 100 to 1000 A cm^{-2}. In some laboratory experiments it has been observed that degradation begins above a current density of 5 to 15 A cm^{-2} at 320° C.

The origin of this discrepancy between the theory and the experiment can be traced to several possible effects. One of them is the intensification of current at the peripheries of non-wetted areas. It has been previously proposed [8] that sodium ion (Na^+) current can be intensified at the peripheries of the areas where the charge transfer resistance across the liquid sodium–β''-Al_2O_3 interface is high. A crack located near a non-wetted area could experience a current density which is much greater than the average current density in the solid electroyte. This effect has been demonstrated [8] with the help of room-temperature blocking experiments. Calculations of current intensification on cracks in samples of finite thickness have been recently made by solution of the Laplace equation [9].

One of the mechanisms by which an area can be blocked to Na^+ transfer across the liquid sodium–β''-Al_2O_3 interface is poor wetting of liquid sodium on β''-Al_2O_3. Our group and many others, working on Na–S battery or Na $|\beta''$-$Al_2O_3|$ Na cells, have observed that the resistance of the cell decreases with time and finally reaches a stable value. This has been generally attributed to the improvement in wetting. Gibson [10], in his attempt to access the wettability of β-alumina by liquid sodium, measured the contact angle between Na and β-Al_2O_3 by the dip-rod technique. He quenched canisters containing a β-Al_2O_3 tube and liquid sodium and measured the contact angles from radiographs taken at room temperature. We have adopted the sessile drop technique to obtain the contact angle of sodium on β''-Al_2O_3 and nasicon [11] which is another super-ionic conductor of sodium with the chemical formula $Na_3Zr_2Si_2PO_{12}$.

Many factors may be expected to affect the

0022–2461/82/030753–07$03.34/0

wetting characteristics of sodium on β''-Al_2O_3. Surface roughness is known to enhance interfacial resistance and it may affect wetting. Moisture has been long known to cause deterioration of β''-Al_2O_3. H_3O^+ can be easily adsorbed by β''-Al_2O_3 from the atmosphere during handling. Hunt *et al.* [12] have shown that considerable moisture remains even when β''-Al_2O_3 is subjected to an annealing treatment in a vacuum at 800° C for many hours. Moisture, as well as some impurities, may affect wetting characteristics and charge transfer resistance. Composition of the liquid sodium, temperature and partial pressure of oxygen may also affect wetting.

In the present work surface roughness of β''-Al_2O_3, composition of liquid sodium and partial pressure of oxygen were kept constant. The major emphasis was on determining the effect of temperature and vacuum annealing treatment on wetting behaviour. The results from wetting experiments have been correlated with the results from Na $|\beta''$-$Al_2O_3|$ Na cell test. The possibility of de-wetting has been examined. Some of the above mentioned experiments were conducted on nasicon as well. The nature of non-wetting was simulated on Na $|\beta''$-$Al_2O_3|$ Na cells to study the effects of wetting on the operation of the battery.

2. Experimental procedure

The criterion for wetting is generally determined by the value of the contact angle, θ, between the liquid and the solid surface. The sessile drop technique was adopted to measure the contact angle of liquid sodium on β''-Al_2O_3. A schematic of sodium drop on β''-Al_2O_3 substrate is given in Fig. 1. The term "completely wetting" is used to indicate that the contact angle is zero. A contact angle of 180° implies "complete non-wetting" of liquid on the solid substrate. "Partial wetting" refers to contact angles greater than zero and less than 180°.

2.1. Sample preparation

Lithia stabilized β''-Al_2O_3 of composition 8.8 wt % Na_2O, 0.75 wt % Li_2O and 90.45 wt % Al_2O_3 was prepared by the procedure described in [13]. Dried $LiNO_3$ and de-agglomerated α-Al_2O_3 were ball-milled and calcined at 1250° C for 2 h to yield $Li_2O.5Al_2O_3$. Subsequently, dried Na_2CO_3 and α-Al_2O_3 powders were ball-milled and calcined at 1250° C to yield a mixture of β-Al_2O_3 and $NaAlO_2$. These two calcined powders were mixed in ratio appropriate for the desired compostion. Circular discs were first die pressed and then isostatically pressed at 2110 kg cm^{-2}. These were sintered for three min at 1600° C in sealed platinum capsules. Specimens were then ground and finally polished on a 60 μm diamond wheel so that surface roughness was uniform in all the discs used. The polished discs were covered with β-Al_2O_3 powder and heated in air at 900° C for 10 h and cooled to room temperature in air. Some of these discs, referred to as "unbaked" in the rest of the paper, were used for contact angle measurement.

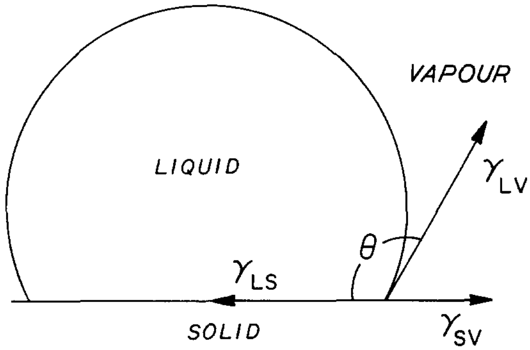

Figure 1 A schematic diagram of the "sessile drop", where γ_{LV}, γ_{SV} and γ_{LS} are the surface tensions at the liquid–vapour, solid–vapour and liquid–solid interfaces respectively.

To study the effect of moisture, some of the "unbaked" discs were "vacuum baked" in the contact angle measurement apparatus at 425° C for 60 to 70 h prior to the introduction of sodium droplets over them. To further examine the effect of moisture on wetting, some of the "unbaked" discs were placed in a 100% relative humidity (r.h.) chamber at room temperature for 24 h. Sodium droplets were then introduced immediately after heating the discs in an argon atmosphere to the desired temperature in the contact angle appartus.

2.2. Contact angle apparatus

The wetting chamber consists of two stainless-steel tubes welded in the form of a cross. The horizontal tube is equipped with quartz windows, one for viewing and the other for background light. Both windows are equipped with baffles to prevent fogging of the windows. The vertical tube has flanges on the tip and bottom and also has attachments for introducing a control thermocouple, an inlet and exit for argon, and fittings to introduce liquid sodium and for evacuation. A

β''-Al_2O_3 disc is placed on a stainless steel platform, introduced through a vacuum fitting welded to the bottom flange. Liquid sodium, placed in a stainless-steel chamber, is forced through a 40 μm stainless-steel filter, a valve and a stainless-steel capillary, under a pressure of argon. A drop of sodium can be easily introduced in a controlled manner. Temperature in monitored with a chromel–alumel thermocouple placed just underneath the platform on which the β''-Al_2O_3 disc is placed.

This chamber is evacuated to 25 millitorr and is heated by a Kanthal furnace built around the chamber. Subsequently an atmosphere of flowing argon is maintained within the chamber. Argon gas is passed through anhydrous $CaSO_4$, over copper turnings at 550° C and bubbled through liquid sodium to dry the argon gas and to decrease the partial pressure of oxygen to a minimal amount. The temperature of the liquid sodium bath is kept the same so that the partial pressure of oxygen during the experiment is constant.

Small drops of sodium of diameter ~ 5 mm were put on the β''-Al_2O_3 discs, subjected to different treatments which are discussed in Section 2.1. The drops were allowed to stabilize and their photographs were taken through the viewing window. The contact angles were determined from the enlarged photographs of the drops. The contact angles of sodium on nasicon were obtained in a similar fashion.

2.3. Na $|\beta''$-$Al_2O_3|$ Na cell tests

One end of a closed β''-Al_2O_3 tube was glass-sealed to an α-Al_2O_3 tube which in turn was sealed to a stainless-steel flange tube assembly. The β''-Al_2O_3 tube–flange assembly was fitted inside a stainless-steel casing which served as a sodium reservoir. The α-Al_2O_3 tube contained a spill over-spout for circulating the sodium. A nickel-plated copper rod inside the β''-Al_2O_3 tube served as one of the electrodes while the stainless-steel casing was the other electrode. The cells were filled with liquid sodium in a similar way as was done for the wetting experiment. A schematic diagram of Na $|\beta''$-$Al_2O_3|$ Na cell is shown in Fig. 2. A d.c. current was then passed through the cells via a d.c. power supply. A switching system was used which reversed the polarities after a pre-set time interval.

To study the effect of baking, some of the tubes in the Na $|\beta''$-$Al_2O_3|$ Na cell tests were vacuum baked for 45 h prior to the introduction of liquid sodium. The cells were operated at a current density of $4\,A\,cm^{-2}$ at temperature of 400° C and the cell resistance was monitored. To simulate high charge transfer resistance, a glass bead was introduced on to the surface of some of the β''-Al_2O_3 tubes. Cells built using these tubes were also tested in a similar manner.

3. Results and discussion

Contact angles of sodium drops on β''-Al_2O_3 ranged, depending on the treatment, from 160°, representing almost complete non-wetting, to 0°, representing complete wetting. This is in contrast to the contact angles obtained by Gibson [10] which were less than 50° in all cases, but complete wetting was not observed. In the experiments of Gibson, cannisters containing molten sodium and β-alumina tubes were quenched. Due to differential cooling, the centre part is the last to cool. Consequently, a typical vortex type of surface, similar to that which would result from freezing of a liquid, must have formed. We believe that for this reason Gibson did not observe as wide a range in contact angle as in the present study.

The sodium drops remained shiny for many hours but became somewhat tarnished after a day. Results of contact angle measurements on β''-Al_2O_3 and nasicon are given in Table I. The error margin in the measurement of the contact angle is $\pm 2°$. Photographs indicating different contact angles are shown in Fig. 3.

3.1. The effect of temperature

As expected the contact angle decreased as the temperature was increased, for any particular treatment given either to nasicon or β''-Al_2O_3. This indicates that charge transfer problems will be reduced at higher temperatures. This is in fact observed in various Na $|\beta''$-$Al_2O_3|$ Na cells.

3.2. The effect of moisture

Moisture seems to have a pronounced effect on wetting. The contact angle of sodium on samples treated in 100% r.h. atmosphere for a day was 90° at 420° C and 103° C; whereas for the unbaked samples the contact angle was 90° at 360° C and 25° at 425° C. The samples which were "vacuum baked" exhibited complete wetting at 360° C an 400° C and an angle of 50° at 200° C. Moisture, either by adsorption or by exchanging H_3O^+ for Na^+ in the structure of β''-alumina close

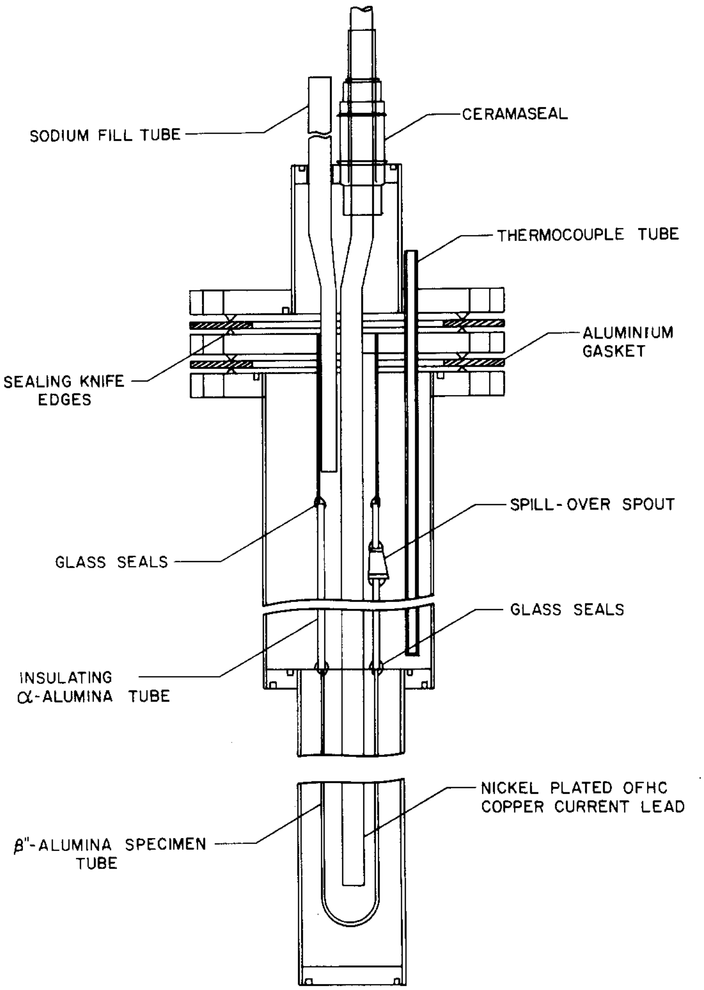

Figure 2 A schematic diagram of the Na|β''-Al_2O_3|Na cell.

TABLE I The contact angle of sodium on β''-Al_2O_3 and Nasicon under various conditions

Material	Treatment	Temperature (°C)	Contact angle (°)
β''-Al_2O_3*	Unbaked	260	160
		360	90
		425	25
β''-Al_2O_3*	Baked at 425° C in	200	50
	vacuum for 60 h	360	0
		400	0
β''-Al_2O_3*	Kept in 100% r.h.	360	103
	at 25° C for 24 h	420	90
Nasicon†	Unbaked	265	128
		355	90
		425	40
Nasicon†	Baked at 425° C in	260	50
	vacuum for 45 h	355	10

*Sintered.
†Hot pressed.

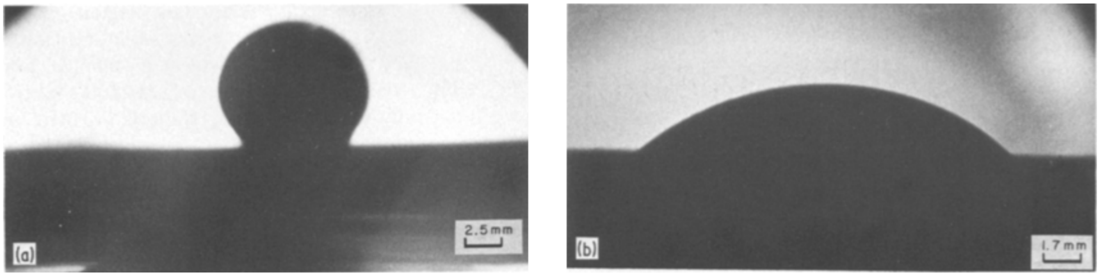

Figure 3 Enlarged photographs of sodium drops on the "unbaked" nasicon surface, with (a) a drop introduced at 265° C showing a contact angle greater than 90°, and (b) a drop introduced at 425° C showing a contact angle less than 90° C.

to the surface, seems to have modified the surface in such a way as to prevent spreading of sodium liquid even at higher temperatures. Presumably, Na_2O or NaOH is formed on the interface between β''-Al_2O_3 and liquid sodium which prevents wetting. This is in agreement with Breiter [14] *et al.*, who have attributed the asymmetric behaviour of certain β''-Al_2O_3 tubes to the formation of a thin passivating film of Na_2O at the β''-Al_2O_3–sodium interface. β''-Al_2O_3 tubes used in a Na–S battery may absorb moisture at the surface while handling and may show a high charge transfer resistance at the Na–β''-Al_2O_3 interface. Baking the disc at 450° C at 30 to 40 millitorrs for two days proved to be very effective. Because of the limitation of the stainless-steel chamber, work at higher baking temperatures could not be undertaken.

3.3. Absence of de-wetting

The sodium drops on β''-Al_2O_3 and nasicon did not exhibit any noticable de-wetting when the temperature was decreased. The surface where a drop had existed was modified in such a way as to improve the wetting of another drop put at the same location. Fig. 4 shows that a sodium drop on that part of the surface where another drop had existed before, exhibits a lower contact angle compared to a drop introduced on the same disc elsewhere.

3.4. Nature of wetted area

The area of the β''-Al_2O_3 disc directly beneath the sodium drop was observed to have turned very dark, as can be seen in Fig. 5. The magnitude of the darkness is lower for the drops that did not wet the β''-Al_2O_3 sample well. The same effect was observed in the case of nasicon. This phenomenon has also been observed when β''-Al_2O_3 tubes were kept in liquid sodium. The depth of penetration of the darkness grows over a period of days. The darkeness observed in these experiments was similar to the darkening observed in the β''-Al_2O_3 tubes used in Na $|\beta''$-$Al_2O_3|$ Na cell testing.

Scanning electron microscopy (SEM) of the area in β''-Al_2O_3 and nasicon directly under Na

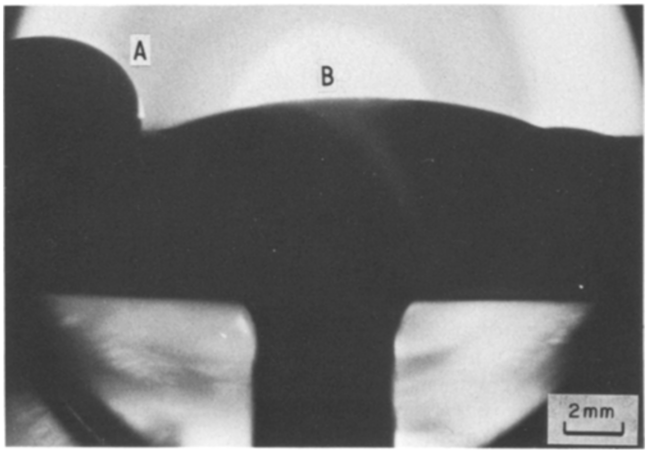

Figure 4 This photograph shows two drops of sodium (A and B) introduced on to a β''-Al_2O_3 specimen at the same time. Drop A was introduced on that portion of the β''-Al_2O_3 specimen which was wetted by sodium earlier. Drop B was introduced elsewhere on the disc. Drop A shows much lower contact angle compared to Drop B. The disc is shown to be resting on a platform. The background shows the diffused light source.

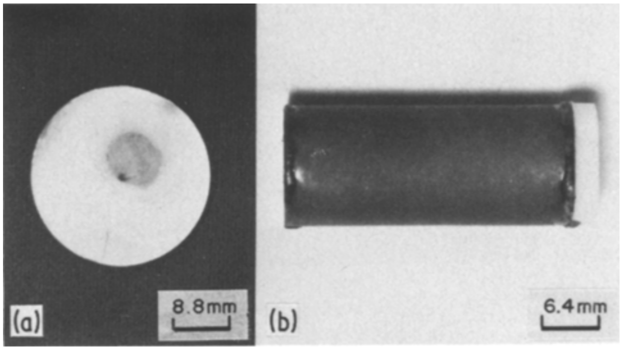

Figure 5 (a) The dark region on the β''-Al_2O_3 disc is the area which was wetted by sodium. (b) Typical β''-alumina tube, which had passed in excess of 1000 A h cm^{-2}, in the Na$|\beta''$-$Al_2O_3|$Na cell, without any signs of degradation.

metal showed that this area was smoother than the rest of the disc (see Fig. 6), suggesting some solubility of β''-Al_2O_3 and nasicon in liquid sodium. Thus the Richman–Tennenhouse model [2] for electrolytic deterioration may well be applicable. In the case of nasicon, generally, cracks were observed to develop directly underneath the sodium drop, as shown in Fig. 7.

3.4. Na$|\beta''$-$Al_2O_3|$Na cells

The detrimental effect of moisture was confirmed in the Na$|\beta''$-$Al_2O_3|$Na cell tests. The cells that were baked at 450° C *in vacu.* for a few days prior to filling with sodium passed, without failure, more than 1000 A cm^{-2} at a current density of 4 A cm^{-2} at 400° C. No change in the cell characteristics were observed. The cells that were not baked out for a prolonged period tended to fail after around 200 A h cm^{-2} under similar conditions. Thus the life of β''-alumina solid electroylte can be enhanced by removing as much moisture as possible.

In some of the Na$|\beta''$-$Al_2O_3|$Na cells, after a glass bead was put on β''-Al_2O_3 tubes, failure occured after a total charge of only 40 A h cm^{-2} was passed. On examination it was found that large cracks emanated from the edge of the glass bead in the form of a star, as shown in Fig. 8. This clearly indicates the effect of blocked areas at the cell operating temperature, and stresses the importance of good wetting.

4. Conclusion

Good wetting of liquid sodium in β''-Al_2O_3 is a necessary condition for low charge transfer resistance across the Na-β''-Al_2O_3 interface which in turn is important for long life of the solid electrolyte as was shown by glass bead experiment in the

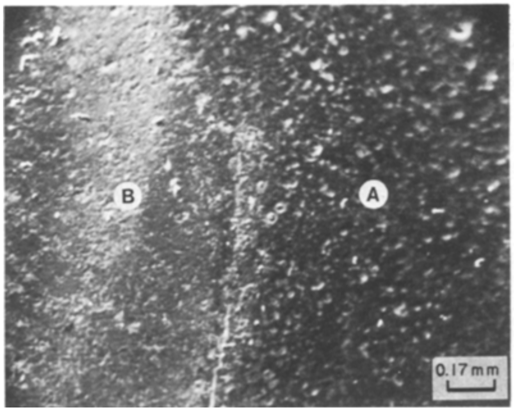

Figure 6 SEM micrograph of β''-Al_2O_3 disc showing the area strained by sodium (B) and the area which was not underneath the sodium drop (A). Region B is smoother than Region A indicating a possible solubility of $\beta''Al_2O_3$ in liquid sodium.

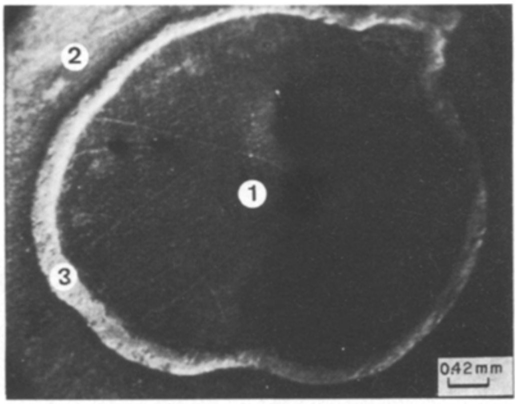

Figure 7 SEM micrograph of nasicon disc that was wetted by sodium drop. Region 1 is where the sodium drop was introduced. Cracks can be seen in this region. Region 2 was not under sodium drop. Region 3 shows a depression on the surface. It represents the periphery of the sodium drop.

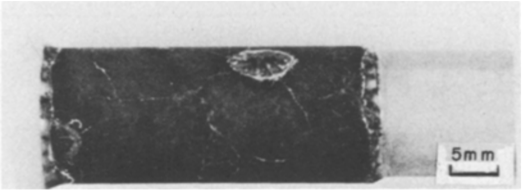

Figure 8 The photograph shows cracks emanating from the periphery of the glass bead, placed on the β''-alumina tube used in Na|$\beta''Al_2O_3$|Na cell test. The glass bead serves as an area of essentially infinite charge transfer resistance, i.e. it simulates non-wetting across the sodium–β''-Al_2O_3 interface resulting in current concentrations on the peripheries. The cell with the glass bead placed on β''-Al_2O_3 passed less than 40 A h cm^{-2} before failure.

Na |β''-Al_2O_3| Na cell test. It was also demonstrated that temperature affects the contact angle. Other parameters remaining constant, contact angle was found to decrease with increasing temperature. It was also shown that moisture can have a detrimental effect on wetting. The contact angle is extremely high when a β''-Al_2O_3 disc was treated with moisture and the contact angle dropped sharply leading to complete wetting when the specimen was baked out in a vacuum at 450° C. The β''-Al_2O_3 disc to which no special treatment was given exhibited intermediate contact angles. The effect of moisture was demonstrated in the Na |β''-Al_2O_3| Na cell tests. Baked out cells passed in excess of 1000 A h cm^{-2} without failure. In the present experiments de-wetting was not observed. Results of the wetting experiments on nasicon were similar to those obtained for β''-Al_2O_3. The experiments suggested some solubility of β''-Al_2O_3 and nasicon in liquid sodium, indicating that the Richman–Tennenhouse model for degradation may be applicable.

Acknowledgement

This work was supported by the U.S. Department of Engergy under Contract Number De-AS02-77ER04451.

References

1. J. T. KUMMER and N. WEBER, *Soc. Automotive Engs. Trans.* **76** (1968) 1003.
2. R. H. RICHMAN and A. J. TENNENHOUSE, *J. Amer. Ceram Soc.* **54** (1975) 63.
3. R. D. ARMSTRONG, T. DICKINGSON and J. TURNER, *Electrochim. Acta* **19** (1974) 187.
4. D. K. SHETTY, A. V. VIRKAR and R. S. GORDON in "Fracture Mechanics of Ceramics", edited by R. C. Bradt, D. P. H. Hasselman and F. F. Lange (Plenum Press, New York, 1977) p. 65.
5. A. V. VIRKAR, *J. Mater. Sci.* **16** (1981) 1142.
6. M. P. J. BRENNEN, *Electrochim. Acta* **25** (1980) 621.
7. L. C. DEJONGHE, L. FELDMAN and A. BUECHELE, *J. Mater. Sci.* **16** (1981) 780.
8. A. V. VIRKAR, L. VISWANATHAN, D. R. BISWAS, *ibid.* **15** (1980) 302.
9. A. WRIGHT, L. VISWANATHAN, A. V. VIRKAR, unpublished work (1981).
10. A. GIBSON, *International Power Sources Symp. 6* (1977) 673.
11. H. Y. P. HONG, *Mater. Res. Bull.* **11** (1976) 173.
12. T. K. HUNT, N. WEBER, T. COLE, in "Fast ion transport in solids", edited by Vashista, Mundy and Shenoy (Elsevier North Holland Inc., Amsterdam 1979) pp. 95-97.
13. G. E. YOUNGBLOOD, A. V. VIRKAR, W. R. CANNON and R. S. GORDON, *Bull. Amer. Ceram. Soc.* **56** (1977) 206.
14. M. W. BREITER, B, DUNN and R. W. POWERS, *Electrochim Acta* **25** (1980) 613.

Received 29 May
and accepted 24 July 1981