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Zirconia-toughened sodium beta″-alumina solid electrolyte

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The effect of a 15 vol% zirconia dispersion on the critical current density for failure initiation of beta″-alumina solid electrolyte was examined. Single phase and composite electrolytes were tested in standard sodium–sodium test cells and subjected to increasing ionic currents. Onset of degradation in the electrolyte was detected by monitoring acoustic emissions from the cell. Preliminary examination of the electrolyte material showed that the problem of producing a uniform dispersion of zirconia in pure beta″-alumina had not been solved. However, the electrolytes were of sufficient quality to draw important conclusions about the potential of transformation toughening for improving electrolyte performance.

1. Introduction

Successful operation of sodium–sulphur batteries depends upon the proper functioning of the solid electrolyte separator, sodium beta″-alumina. One of the factors that can limit cell life is electrolytic failure of the electrolyte. Since such failure involves the initiation and propagation of a sodium-filled crack from the surface of the electrolyte, strength and fracture toughness of the material play important roles [1–7]. Zirconia dispersions have proved to be effective in strengthening and toughening various ceramics, and should also be effective in sodium beta″-alumina solid electrolytes [8–12].

Strengthened electrolytes should therefore exhibit higher critical current densities for failure initiation, higher tolerance for mechanical stress, and lower requirements for separator thickness. The present paper describes some measurements of the critical current densities observed on a first generation of zirconia dispersion-toughened sodium beta″-alumina solid electrolytes. While the microstructure of these electrolytes was quite imperfect, the results indicated that dispersion toughening offers advantages for sodium beta″-alumina electrolytes.

2. Experimental methods and results

The onset of crack propagation in a solid electrolyte can be detected with an acoustic emission sensor [13, 14]. When cracks propagate through a solid they release bursts of elastic energy which travel through the test cell in the form of acoustic waves [15]. These waves can be directed to a piezo-electric transducer through a dense-media guide. The resulting electrical signals then can be processed and filtered according to various parameters, such as amplitude, frequency, and slope. The sensitivity of this method for the detection of mode I degradation has been experimentally confirmed [13, 14].

The sodium–sodium test cell apparatus for evaluating the toughening effect is shown in Fig. 1. The molten sodium bath was contained in an alumina crucible located within the heating zone of the furnace. Current was imposed through the electrolyte by a programmed galvanostat/potentiostat.

Prior to testing, the electrolyte was ultrasonically cleaned in ethanol, and baked in a furnace at 800° C for 30 min to drive off moisture and remove organic material from the surface. During the baking procedure, the electrolyte was packed in beta″-alumina powder to prevent soda loss. The electrolyte was then sealed to the bottom of an alpha-alumina tube with a glass of a closely matched coefficient of thermal expansion. The acoustic emission transducer was attached to the tube with an alpha-alumina waveguide. The entire assembly was contained in an argon atmosphere glove box, containing less than 1 p.p.m. oxygen to minimize oxidation of the sodium.

Conditioning of the cell was necessary to ensure complete wetting of the electrolyte. A properly wetted electrolyte will exhibit low interfacial resistance and a near-uniform current distribution across the test surface. This condition was obtained by electrolytically filling the cell with sodium. To prevent degradation of the electrolyte during the conditioning stage, the cell was filled at low current densities, typically $10\,\mathrm{mA\,cm^{-2}}$, for 24 h.

At this point, the cell resistance was between 1 and $3\,\Omega$ (at 300° C), and the actual testing of the cell was begun. To initiate mode I degradation [6, 7], a gradually increasing current was forced through the cell. As the mode I cracks began to propagate through the electrolyte, they were detected by an acoustic emission transducer.

After completion of the testing, the electrolytes were examined to confirm that degradation had occurred. The electrolyte was removed from the glovebox and immersed in methanol to dissolve any sodium adhering to its surface. The electrolyte was

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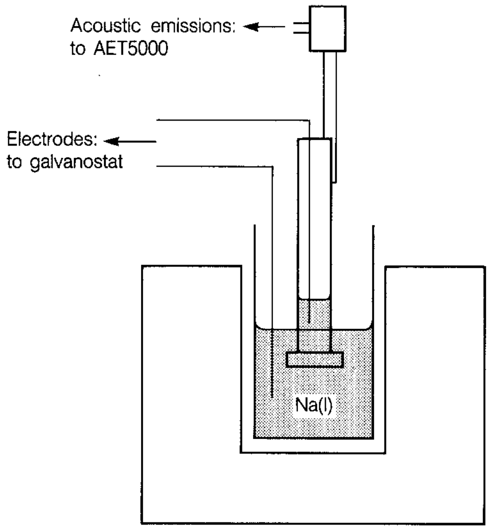

Figure 1 Experimental apparatus.

then cut from the alpha-alumina tube and stained in a silver nitrate solution [16]. Sodium-filled cracks in the electrolyte could then be identified by optical microscopy.

Data for the acoustic emission tests were collected in the form shown in Fig. 2. The onset of cracking was accompanied by a sharp increase in acoustic emission activity over the background.

Single phase beta″-alumina electrolytes were provided by Ceramatec (Salt Lake City, Utah) and zirconia dispersion toughened electrolytes were provided by Rockwell Int. (Thousand Oaks, California).

The presence of large grains or agglomerates of either zirconia or beta″-alumina can be detrimental to the performance of the electrolyte. Because of differential densification rates during the electrolyte fabrication, agglomerates may create large pores in the final product [12].

The commercially available powders used in the fabrication of the test specimen had been examined by Rockwell International to determine the size distribution [12]. For the most part, the particles were submicrometre, but a significant number of agglomerates as large as 20 μm were present. To remove these agglomerates, the powders were ultrasonically dispersed and sedimented in a centrifuge.

Combination of zirconia and beta″-alumina powders into a stable suspension proved difficult. Although beta″-alumina powders could be dispersed in many different alcohols, zirconia was found to flocculate in the same dispersion media [12]. During the initial sedimentation phase, the zirconia powder was necessarily dispersed in water (pH = 2.5). This medium is not suitable for sodium beta″-alumina, as water will leach sodium out of the material. The most stable slip of both powders that could be maintained under these circumstances was in ethanol with ultrasonic agitation.

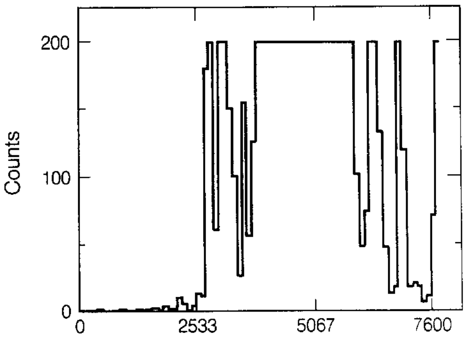

Figure 2 Acoustic emission output. The sharp increase in counts corresponds to the onset of crack growth.

The next step in the fabrication process was to pour the slip on to a plaster of paris mould, followed by drying under flowing argon. This precaution was necessary because of the sensitivity of sodium beta″-alumina to water. The dried specimens were then sintered at 1535° C for 1 h.

The surfaces of the electrolytes were prepared in two different ways. One population was left in the as-sintered state, while the other was polished to a mirror finish. This finish was obtained by grinding on diamond wheels (60, 33 and 6 μm), with a final polishing on 3 μm diamond paste impregnated on paper lubricated with kerosene.

Specimens from the four populations (single phase as-sintered, single phase polished, toughened as-sintered, and toughened polished) were tested. The bulk microstructure of each group was examined by sectioning and polishing each sample. The microstructural features were enhanced by thermal etching at 1400° C for 10 min.

The bulk of the toughened specimens (Fig. 3a) showed serious departures from the desired microstructure. Large alumina particles, grey or dark in the micrographs, were present together with zirconia agglomerates (white). Adjacent to these particles were voids which arose from the differential sintering rates of the two materials.

A cross section of the pure specimens (Fig. 3b) showed a bimodal distribution. The majority of the grains were of the order of 1 μm, but some large tabular grains up to 20 μm in length had developed during sintering.

The zirconia agglomerates may have resulted from the instability of this powder in the dispersion medium. As large amounts of the zirconia were collected in the agglomerates, these were zirconia deficient regions in the electrolyte where no toughening could occur.

A significant microstructural feature was that the grain size of the beta″-alumina had been reduced by the zirconia dispersion. The toughened microstructure lacked the large beta″ grains found in the monophase material.

Examination of surface of the as-sintered specimens showed further deviations from the desired microstructure for the toughened material (Fig. 4a). Here, as in the bulk, large particles and agglomerates were present which gave rise to voids in the structure. Overall, the surface of the toughened material exhibited more pores betrween individual grains than the single phase electrolyte (Fig. 4b).

The polished electrolytes were much more alike in surface structure (Fig. 5). Polishing had evened out the excessive surface roughness of the toughened

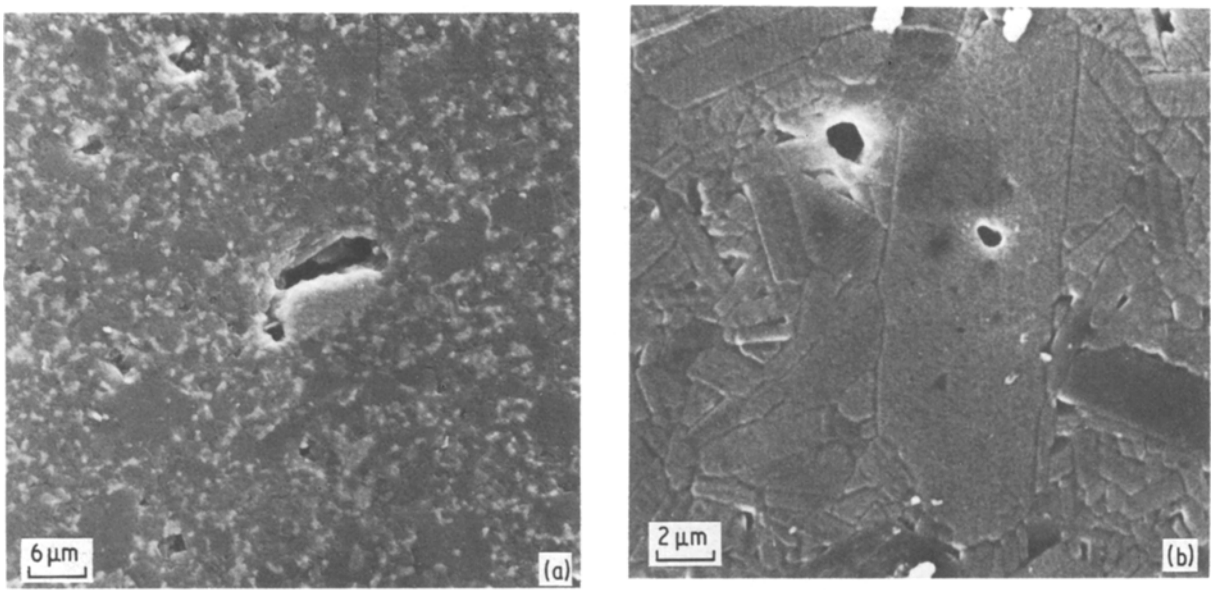

Figure 3 Cross sections of the electrolytes: (a) toughened material. Differential sintering of the alumina particles (dark), zirconia agglomerates (white), and the matrix have led to voids in the microstructure; (b) single-phase material, showing the bimodal distribution of grain sizes.

ceramics. It is likely, however, that the polishing had introduced microscopic cracks to both surfaces that were too small to be imaged in the scanning electron microscope.

Polishing of zirconia-toughened electrolytes should induce the toughening reaction in a surface layer. The mechanical stresses expended during the polishing process should be sufficient to overcome the energy barrier constraining the zirconia particles in the surface layers, and initiate the transformation of the tetragonal to the monoclinic phase.

Microscopic cracks, created during polishing, will be subjected to compressive stresses by the transformed zirconia dispersion. These cracks will experience the maximum increase in fracture toughness predicted by McMeeking and Evans [10] as the crack faces will be entirely contained within a zone of transformed zirconia dispersion. The polishing procedure, while creating a higher surface flaw population, should also induce a compressive layer, opposing crack propagation from the electrolyte surface.

Examination of the surface of the electrolytes was necessary to ensure the polishing had introduced a compressive surface layer. An X-ray diffractometer was used to determine the crystal structure present in the surface layer of the specimens. For the purposes of this study, the X-ray scattering with 2θ between 25° and 35° was examined. Within range, the $(1\,1\,\bar{1})$ ($2\theta = 28.2°$) and $(1\,1\,1)$ ($2\theta = 31.5°$) reflections of monoclinic zirconia, and the $(1\,1\,1)$ ($2\theta = 30.2°$) of tetragonal zirconia are found.

The X-ray scans in Fig. 6a (as-sintered) and b (polished) show the effect of the polishing process on the relative amounts of the phases. In going from the as-sintered to the polished cases, the intensity of the $(1\,1\,\bar{1})$ peak of monoclinic zirconia increases by nearly an order of magnitude. This indicates that by subjecting the surface to the stresses of polishing, the toughening transformation occurs in the surface layer.

The fracture toughness of the electrolytes may be determined from microhardness indentations [17, 18]. This method indicated fracture toughnesses of

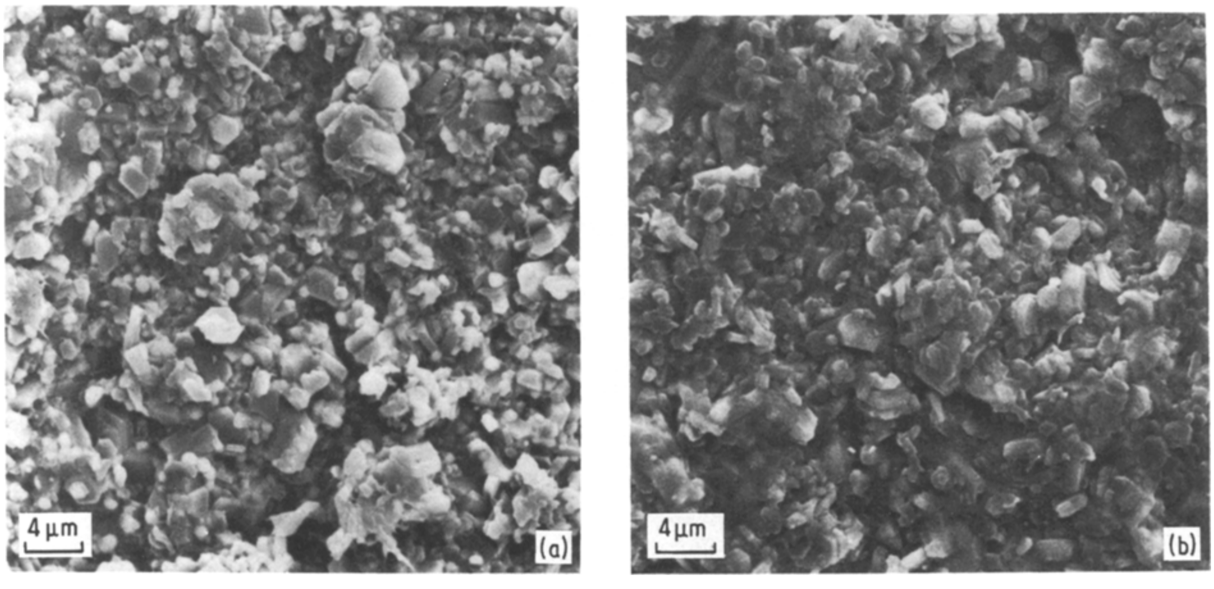

Figure 4 As-sintered surfaces: (a) toughened electrolyte. The surface shows considerably more roughness than the single phase surface (b).

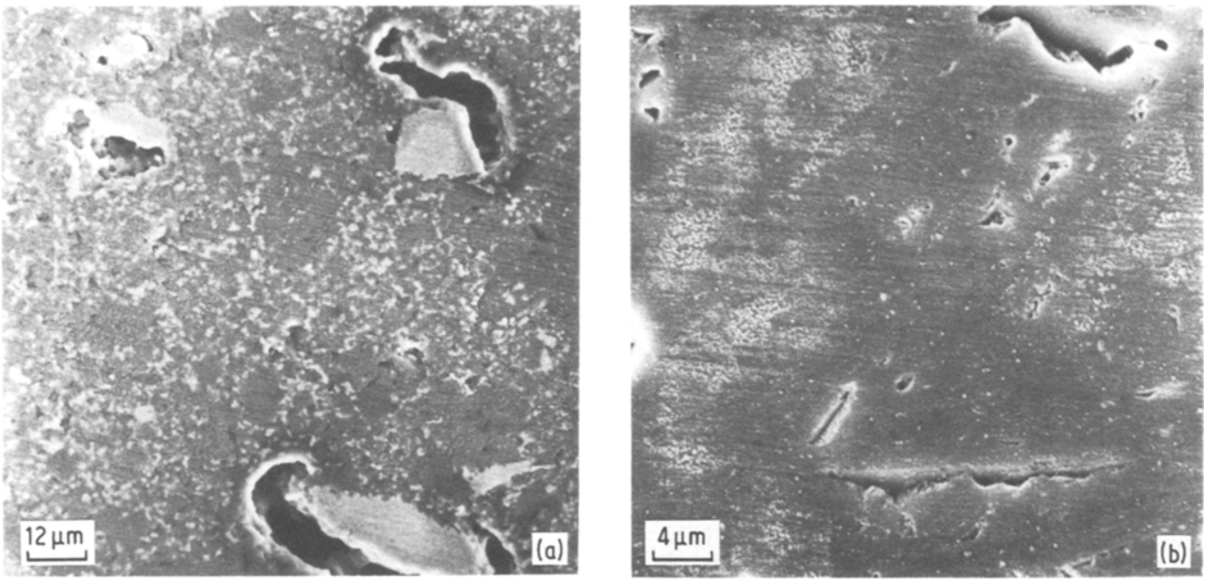

Figure 5 Polished surfaces of the toughened (a) and single-phase (b) electrolytes.

3.0 MPa m$^{1/2}$ for monophase beta″-alumina and 3.7 MPa m$^{1/2}$ for the composite electrolyte. A number of authors have predicted that the critical current density for Mode I crack initiation is proportional to the fourth power of the fracture toughness, K_{Ic}, of the electrolyte [4–6]. Using this relationship, the measured increase in K_{Ic} would yield a 134% improvement in the critical current density of the electrolyte. However, these promising fracture toughness values must be qualified. The hardness indentations extended over approximately of 50 μm and therefore gave only a local fracture toughness of the composite. This type of measurement is not representative of the total flaw population sampled by the ionic current. The critical current density is extremely dependent on the condition of the entire electrolyte surface. Therefore, the measurements, obtained in "good" regions of the surface, did not reflect the extreme values of the total flaw population.

Pure beta″-alumina also suffers from local variations in the fracture toughness. Single grains of the matrix material exhibit severe variations in this

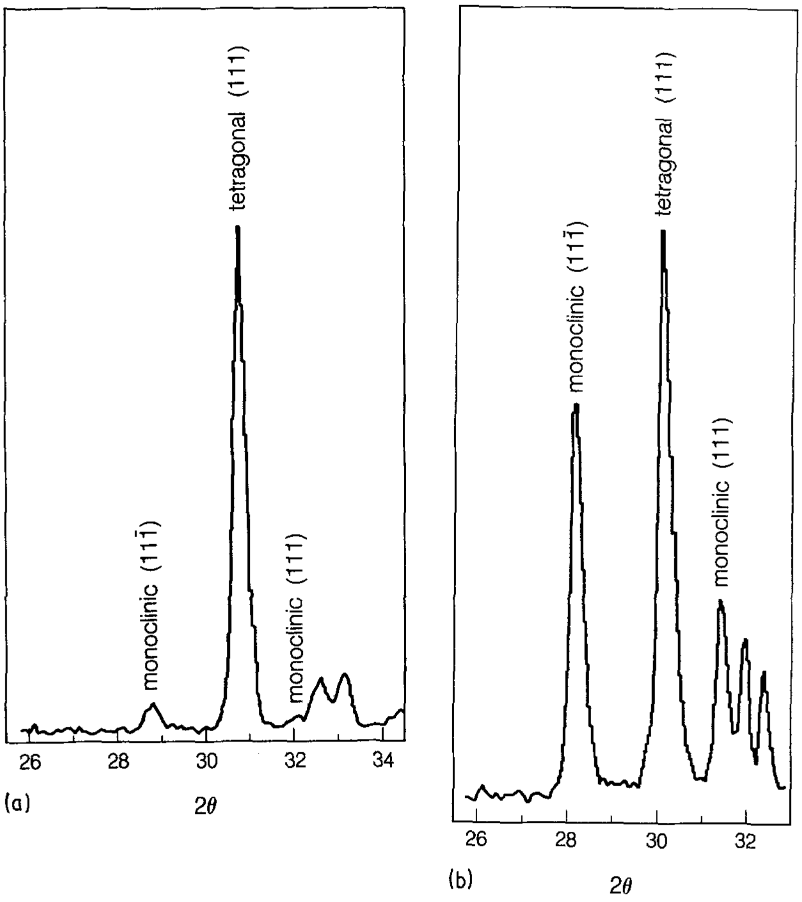

Figure 6 X-ray diffractometer scans of as-sintered (a) and polished (b) surfaces of the toughened material. The polishing has induced the tetragonal to monoclinic transformation, as shown by the increase in the monoclinic peak.

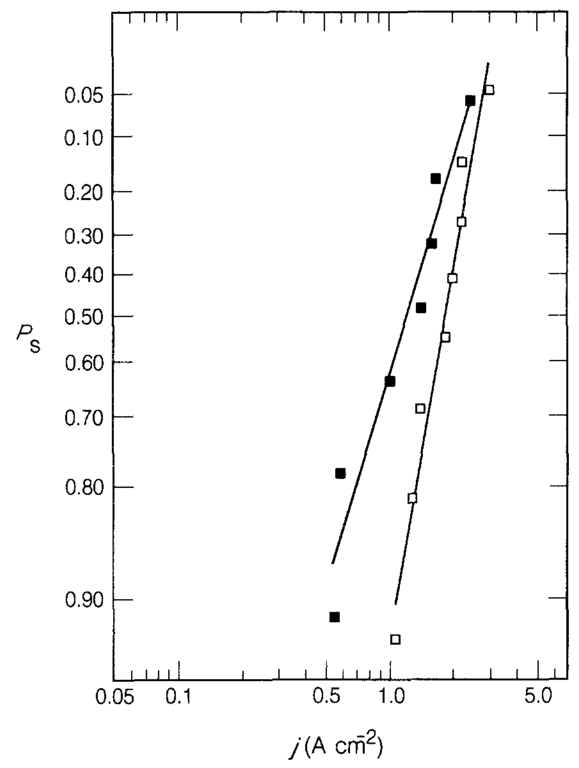

Figure 7 Weibull distributions of the as-sintered populations. The toughened electrolyte shows a lower survival probability (P_s) than does the single-phase material. (■) Toughened as-sintered; (□) single-phase as-sintered.

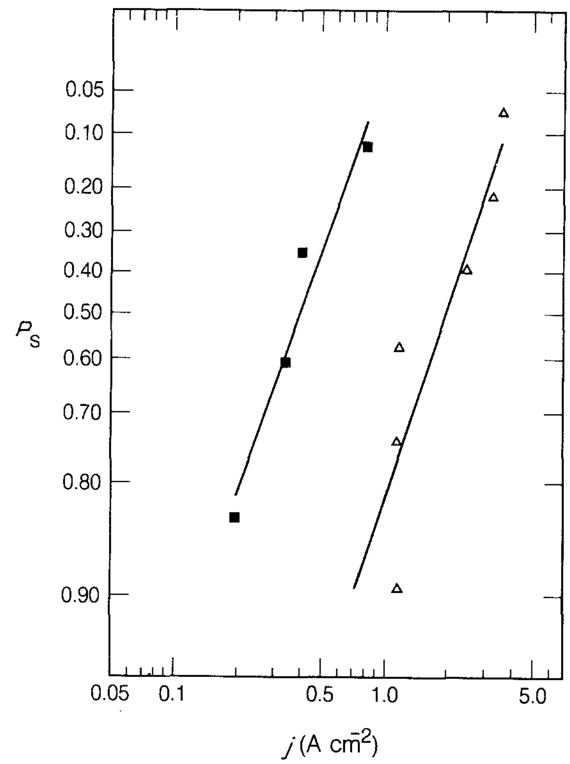

Figure 8 Weibull distributions of the polished populations. The toughened electrolyte now shows improved performance compared to the single-phase material. (△) Toughened-polished; (■) single-phase polished.

material parameter because of the weak bonding across the basal planes [18]. Thus, the monophase electrolyte may also present much lower local values of K_{Ic} to a propagating crack than would be indicated by indentation measurements.

3. Discussion

3.1. As-sintered surfaces

The Weibull distributions of the current densities at which Mode I failure was initiated for the as-sintered populations are shown in Fig. 7. Contrary to expectations, the toughened electrolyte showed a *decrease* in performance compared to the pure case. This would be surprising in light of the fracture toughness measurements, but not on the basis of the microstructural characteristics of the imperfect composite. Also, zirconia does not possess the ionic conduction characteristics of beta″-alumina. Zirconia agglomerates on the surface of the electrolytes will present blocking regions, preventing sodium ion conduction. These blocking regions concentrate the ionic current around the perimeter of the agglomerates, already a weak portion of the microstructure. The existence of blocking regions in beta″-alumina has been associated with the accelerated degradation of the electrolytes [5].

The non-conducting second phase will, on average, also cause higher current densities in the composite material. For a given current, there is 15% less beta″-alumina available in the composite electrolyte for the transport of sodium ions. The higher current density in the conducting phase will lead to lower over-all critical current densities, as measurements assume equal volumes of conducting material.

The disadvantages associated with the presence of a non-conducting phase in the electrolyte should, however, be overcome by the toughening effect of the zirconia dispersion. Unfortunately, as shown in Fig. 3a, the dispersion, which is very sensitive to processing, was not of optimum quality.

The agglomeration of the toughening phase created large regions where no zirconia dispersion existed. These regions still exhibited the severe surface flaw population of the composite electrolyte but without the benefit of a toughening phase, and were especially susceptible to crack initiation.

3.2. Polished surfaces

The results for polished electrolytes, shown in Fig. 8, conform better to the expectations. The toughened ceramic showed a substantial increase in performance over the single phase material. Although the dispersion was not of high quality, the microhardness measurements indicated a signficant increase in the fracture toughness of composite versus single phase electrolytes. The differences in the surface condition were diminished by the polishing, allowing the toughening effect of the second phase to emerge.

The reason for the dramatic increase may be found in the damage associated with the polishing step. Microscopic cracks are introduced during this procedure. In the case of single phase beta″-alumina, these cracks remain to provide Mode I initiation sites during testing of the electrolyte. The toughened electrolytes possess much different characteristics. The surface flaw population generated by polishing the toughened material resides within the transformation zone, and therefore will experience the toughening increment.

It is evident from the results shown here that polishing the toughened electrolyte, by inducing the toughening transformation in the surface layer, will oppose incurred surface damage, at the same time reducing the criticality of pre-existing surface cracks. The toughening characteristics of the second phase make the composite material much less sensitive to surface damage caused by handling. Thus, in spite of the imperfect microstructure of this first generation of zirconia dispersion-toughened electrolytes, the advantage of being less sensitive to accidental surface damage is evident. It is also clear that improved processing could yield toughened electrolytes of superior resistance to Mode I failure.

4. Conclusion

Because of the quality of the toughened electrolytes tested, the correlation between the increase in fracture toughness and increase in cell performance was not immediately obvious. However, when some of the deficiencies of the toughened electrolytes were removed by polishing, an increase in critical current density was observed. This improvement was large enough to surpass the performance of the single phase, as-sintered electrolytes.

Even more significant was the strong improvement in performance of the polished composite over the polished monophase electrolyte. This indicated that the toughening dispersion not only increased the fracture toughness of the material, thereby increasing the critical current density, but also enabled the electrolyte to resist surface damage introduced during cell assembly and handling.

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