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SOLID ELECTROLYTE DEGRADATION: PROBLEMS AND SOLUTIONS

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SOLID ELECTROLYTE DEGRADATION: PROBLEMS AND SOLUTIONS

Lutgard C. DeJonghe

In this paper our present understanding of degradation phenomena in sodium beta aluminas is reviewed. The theories and experimental results permit the formulation of suggestions for further electrolyte and cell development that could lead to improved battery performance. The indications are that conditions exist where degradation of the electrolyte itself may be avoided.

INTRODUCTION

Examination of sodium beta"-alumina solid electrolytes after their use in sodium/sulfur cells reveal a variety of progressive changes. These changes can be summarized in four categories:

1. Darkening of the electrolyte in contact with the sodium electrode: chemical coloration
2. Sodium precipitation in the interior of the electrolyte: Mode II degradation
3. Cracks penetrating the electrolyte and causing total or partial short circuits: Mode I degradation.
4. Cracking and electrode imprinting on the sulfur side of the electrolyte: sulfur side attack.

I like to review each of these phenomena, give my current understanding of them, and present some possible solutions and suggestions that would, based on theoretical as well as on experimental results, lead to improved performance of the electrolyte itself. A difficulty in the development of the understanding of degradation phenomena in these solid electrolytes has been that there is an interaction between a number of effects. For example, while the chemical coloration in itself is of no consequence in the functioning of clean electrolyte under normal cell operating conditions, it may play a role in degradation when the electrolyte becomes contaminated, or it may participate in stimulating slow crack growth.

This review is only an overview of the work performed by our group at LBL under DOE and EPRI sponsorship. It is therefore biased towards our interpretation of degradation phenomena. Since this review attempts to present our current understanding, some work has not yet reached the stage of inclusion in reports or publications.

CHEMICAL COLORATION

When sodium beta- or beta"-aluminas are in contact with molten sodium at normal cell operating temperatures, a darkening develops in the electrolyte progressing in a more or less layer-like fashion, with a parabolic time dependence. The rate constant, K in the expression $\delta^2 = 2Kt$, where δ is the darkened layer thickness and t is the time, depends significantly on the electrolyte composition. Further, in polycrystalline sodium beta"-alumina, this darkening proceeds preferentially along grain boundaries (1). It is now fairly well established that this discoloration effect involves the partial reduction of the solid electrolyte by the sodium electrode (2). The oxygen vacancies that are introduced are compensated by electrons, leading to a somewhat higher electronic conductivity in the discolored region compared to virgin electrolyte. The increased electronic conductivity is difficult to measure at cell operating temperatures. It is about two orders of magnitude above the intrinsic electronic conductivity (3,4), and thus it does not affect the Faradaic efficiency of the cell in any measurable way. The involvement of a reduction reaction implies that the oxygen ions are to some extent mobile. On the basis of the measured coloration kinetics one could make a fair estimate of the effective oxygen diffusion coefficient. This works out to about $2 \times 10^{-16} \text{ cm}^2/\text{sec}$ for an electrolyte with a 1.1 micrometer grain size, assuming that 1/2 of the grain boundary oxygen gets removed by the reduction process. This in turn can be used to estimate the oxygen ion conductivity with the Nernst-Einstein relation, giving, at 300°C an approximate oxygen ion conductivity of $4 \times 10^{-13} (\text{ohm.cm})^{-1}$. This estimate has been made assuming oxygen transport along grainboundaries predominates, as the coloration results on polycrystalline beta" aluminas indicate (1). This puts the oxygen ion conductivity for the grainboundary reduced beta"-alumina in the neighborhood of the electronic conductivity. The experiments on the chemical coloration show, however, that oxygen diffusion is rate controlling. Since the electronic conductivity is around $1 \times 10^{-13} (\text{ohm.cm})^{-1}$ for the discolored beta", at 300°C, the estimated oxygen conductivity is probably somewhat high, but is not expected to be more than one order of magnitude below the electronic conductivity. The coloration results and the ionic conduction estimates thus indicate that the oxygen ions have a non-negligible mobility. This may be of significance in slow degradation phenomena.

While the static chemical coloration produces no other physical effects than a minor reduction and increase in the electronic conductivity, it must be pointed out that the oxygen fugacity in the sodium electrode determines how reducing the sodium really is. The oxygen fugacity at the interfaces between the sodium and the electrolyte thus plays an important role in determining the degree to which the electrolyte may be reduced. It is then interesting to note that at the sodium exit surface the oxygen fugacity should drop during sodium electrolysis, while at the sodium entrance side it should rise. This is due to the oxygen removal and oxygen accumulation at these respective interfaces when current is passed. The sodium that is produced at the Na exit side is completely oxygen free, so that the interface oxygen concentration should drop without limit. It can be shown that the surface oxygen concentration, C_s , follows the relationship:

$$C_s = C_\infty \{1 - \text{erf}(\Omega_{\text{Na}} Jt / F\sqrt{Dt})\} \quad (1)$$

where C_s is the oxygen concentration in the sodium adjacent to the sodium exit surface, C_∞ is the oxygen concentration in the electrode at infinity (i.e. the dissolved oxygen content), Ω_{Na} is the molar volume of sodium, J is the charging current density, F is Faraday's constant, D is the oxygen diffusivity in the sodium electrode, and t is the time. This continuous drop in the oxygen concentration at the sodium exit side should eventually cause destructive reduction of the electrolyte with which it is in contact, with an associated rise in the interface resistance as the lattice gets progressively destroyed. An indication of this effect may be seen in the more intense discoloration that develops at the sodium exit surfaces of electrolytes used in one-way Na/Na tests. Such destructive reduction should be found especially near Mode I crack tips, where fresh sodium is continuously formed at a relatively high local rate during cell charging.

INTERNAL SODIUM DEPOSITION: MODE II DEGRADATION

In some used electrolytes evidence was found of a progressive internal deposition of metallic sodium (5). This is, however, not a common observation, and most electrolytes that we have examined are free of this form of degradation. The internal deposition of metallic sodium is the consequence of sending currents through an electrolyte that contains a gradient in the electronic/ionic transport number ratios. The resistance overvoltages required to produce the Mode II degradation are estimated to be 3 to 5 times those that are normally encountered in the Na/S cell (6). However, when impurities or destructive reduction lead to a simultaneous decrease of the ionic conductivity while the electronic conductivity is rising, as is possible in the reduction layer that develops as a result of electrolyte contact

with a contaminated sodium electrode, Mode II degradation could more easily be initiated (7). It is interesting to note in this context that considerably heavier damage was found in the sodium side surface layers of electrolytes that showed evidence of calcium contamination. Calcium is indeed an impurity that strongly reduces the ionic conductivity of sodium beta-aluminas. It is clear from such considerations that contamination of the cell, either as a consequence of fabrication or of operation, must be kept to an absolute minimum. Quantitative impurity limits are needed but cannot yet be established with confidence. This is an area where a continued research effort will be necessary.

RAPID AND SLOW CRACK GROWTH: MODE I DEGRADATION

The aspects of rapid crack growth in solid electrolytes driven by Poiseuille pressures developed by Na that is cathodically plated in the crack, has been dealt with in some detail by Virkar in this Workshop. Of significance is that an approximate, but reasonable, three dimensional model that considers the current to focus on a ribbon shaped rather than on a penny shaped crack, leads to estimates of the critical current density for catastrophic crack propagation that start to approach realistic values (8). A problematic aspect of all the catastrophic Mode I calculations is that the critical current densities that are estimated for crack propagation all depend very sensitively on how the crack opening is affected by the pressure generated in the crack. It is difficult to see how this problem can be circumvented. One can, however, state with some confidence that this mode of crack propagation is operative at relatively high current densities when rapid failure occurs, and that the critical current densities are proportional to the fracture toughness raised to the fourth power (8,9,10). Improving the electrolyte fracture toughness is thus an important step towards better electrolyte performance. Cell design and operating conditions should be such that the current densities necessary for catastrophic crack propagation, typically ranging up to several amps per cm^2 , do not occur. In the initiation stages, the crack may be propagated at considerably lower current densities. This is evident from our acoustic emission detection studies (11). Recent work has shown that when the crack is on the order of the grain size, weak grainboundaries become very important (12), and that fracture toughness anisotropy may lead to critical stress intensity factors that are a factor of ten lower than the ones derived from macroscopic fracture mechanics measurements (13). Thus, it is possible for cracks to initiate at relatively low current densities, say 200 mA/cm^2 with a Weibull modulus of 2 describing the statistical spread, and then to propagate catastrophically at high current densities. The results indicate clearly that very large grains, such as resulting from abnormal grain growth, should be avoided to suppress crack initiation (11, 12).

An important finding on electrolytes that have been used for some time in Na/S cells is that there is evidence of a slow crack propagation mechanism. This follows from an analysis of the chemical coloration profiles around cracks found in used electrolytes. Two phenomena may lead to slow crack propagation at current densities well below catastrophic, rapid failure: one is the destructive reduction, the other is the Mode II degradation mode that may deposit sodium ahead of the crack tip. In the Mode I-Mode II coupling, the appearance of electronic conduction ahead of the crack tips due to a localized electrolyte reduction by the sodium, can lead to deposition of sodium in front of the crack tip, thus lowering the stress at which a crack will propagate (14). The instant that the sodium starts depositing should depend on how fast the layer, of increased local electronic conductivity, and of thickness δ , develops ahead of the crack tip. Thus, slow crack propagation rates should be linked to the coloration rate. If one expects that the Mode II can precipitate sodium ahead of the crack tip, then microstructural observations on samples in which slow crack growth occurred would indicate that the discolored layer of increased electronic conductivity is no more than about 10 to 15 micrometers thick at the crack tip. It can then be assumed that this is the thickness, δ , at which Mode II starts precipitating sodium. This would cause the crack to advance rapidly by a distance about equal to δ , and the process would then repeat. As a result, the crack propagates at a rate that is on the order of $v=K/\delta$, where K is the scaling constant in the layer growth kinetics expression $\delta^2 = 2Kt$. With the values of K determined for sodium-beta" alumina of a 1.1 micrometer grain size, (1) this would lead to $v \sim 10^{-6}$ cm/sec. The coloration profiles around some cracks would lead us to deduce crack velocities of this order of magnitude. Note that this mechanism depends again on the fracture toughness of the electrolyte.

In case destructive reduction is rate controlling, at still lower current densities, the rate of crack propagation should be still lower. Measurements on the dependence of the average critical current density on the rate of current increase would indicate that such cracks would propagate with a minimum rate of about 30 micrometer per year.

It can thus be tentatively concluded that there are several domains of current density where sodium filled cracks can propagate at significantly different rates, driven by different propagation mechanisms. At the low current densities, destructive reduction at the crack tip is likely to be involved. At intermediate current densities, Mode I/Mode II coupling at the crack tips could lead to a faster sub-critical crack propagation. Finally, at high current densities, equal to or

exceeding the critical current density, rapid, catastrophic crack propagation occurs.

It should be noted that in all modes of crack propagation the fracture toughness of the electrolyte enters as an important parameter. The critical current density and the crack velocities thus depend very significantly on the intrinsic mechanical strength and fracture toughness of the electrolyte. A continued effort should thus be made to increase the fracture toughness of the ceramic electrolyte, keeping the ionic conductivity as high as possible.

SULFUR SIDE ATTACK

When sodium-beta and beta" aluminas are immersed in sodium polysulfides, chemical attack seems to occur rather rapidly when x in Na_2S_x reaches into the two phase region in equilibrium with Na_2S_2 . Thus, it is the discharged sulfur electrode composition that is the most corrosive one. As a result, attention should be devoted to management of the discharge current and cutoff voltages, as well as to the structure of the sulfur electrode. It is particularly where graphite fibers touch or are very near the electrolyte, that these corrosive compositions, possibly with formation of some solid Na_2S_2 , might occur. Most electrolytes that have been tested by cell manufacturers show evidence of this sulfur side attack, taking the form of an "imprinting" of the sulfur electrode graphite filler (1). Recent results obtained by some cell developers show, however, that the sulfur side degradation can be suppressed. It is likely that further development of the sulfur electrode and cell cycling history will avoid sulfur side degradation altogether, if these points are taken into consideration.

RECOMMENDATIONS

The results of laboratory investigation and of the cell developers indicates that progress can be made towards developing electrolytes, cell design and cell operating conditions that minimize or even avoid altogether electrolyte degradation phenomena for several years of cell operation.

Based on the results discussed in this presentation, it is now possible to formulate some practical recommendations for further cell developments that should lead to improved electrolyte performance:

- a. electrolytes should have as high a strength and fracture toughness as possible
- b. cell contamination should be kept to a minimum

- c. electrolyte resistance should be as low as possible
- d. electrolytes should be developed for which the coloration rate and destructive reduction rates are lowest.
- e. the structure of the sulfur electrode and the discharge current densities should be controlled, so that the local corrosive electrode compositions will be avoided.

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