

ELECTROLYTE CREEPAGE IN GALVANIC CELLS I. CONTRIBUTION TO THE PHENOMENA

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Summary

The subject of this investigation has been electrolyte creepage, a phenomenon which is held responsible for leaking of alkaline cells. Experiments show that the driving force is the electrochemical reduction of water or oxygen at the negative current collector. The electrolyte film contains a higher concentration of alkali than does the bulk electrolyte from which it is generated. The visible film is generated by condensation of water vapour. Investigations on the different behaviour of ions show that potassium apparently moves faster than sodium; anions in the bulk electrolyte do not take part in film formation.

Experiments show that two mechanisms might lead to leaking cells. One is an apparent leakage through pores, which can be suppressed by high pressure, smooth surfaces and pore plugging materials. The second effect is of an electrochemical nature. It cannot be prevented by usual means.

Introduction

Over the last ten years galvanic elements with alkaline electrolyte have claimed an ever increasing share of the market. These cells combine high energy- and power-to-volume ratio with comparatively low prices. Unfortunately, after some time the cells start leaking. Leakage of electrolyte almost always occurs at the negative current collector. This appearance is attributed to the phenomenon of electrolyte creep. Former publications [1 - 3] have cited the wetting between electrolyte and the strongly negative polarised current collector as the reason for the leakage. Later it was reported [4, 5] that a special treatment of the surface of some metals, especially a mild oxidation that results in an epitactic layer of oxide, can largely suppress the leakage. At present, no fully satisfactory explanation for electrolyte creep can be given.

Based on earlier published work [5 - 8] we have tried to advance our knowledge concerning the phenomenon of electrolyte creep, and to develop ways and means of preventing cells from leaking.

Experimental

Electrolyte creep can be demonstrated by a very simple experiment. If a strip of metal is partially inserted into a solution of alkali hydroxide and this metal is externally polarised by a cadmium- or zinc electrode, for example then within a very short time a film of electrolyte will appear on the strip of metal. On nickel, this film reaches a height of 1 - 2 cm within 24 h. This value depends on a number of parameters such as the electrolyte itself, its concentration, the potential, the surrounding atmosphere, the roughness, etc. When no negative potential is applied to the strip no film is observed. The same force that generates the film is held responsible for the leakage of alkaline cells.

A strip of nickel was tempered in hydrogen and placed in an apparatus similar to that described by Hull and James [6]. This operation was carried out in a glove-box under oxygen-free argon. The lower part of the probe was inserted into 6N KOH. Its potential could be controlled *via* an external potentiostat and a working electrode (cadmium-sinterfoil). The atmosphere inside the apparatus consisted of a mixture of 95% argon and 5% hydrogen. The nickel strip almost showed the potential of the reversible hydrogen electrode, which is a few millivolts more negative than the cadmium potential. After 24 h at the cadmium potential there was no visible electrolyte film on the nickel strip (other than the usual meniscus).

The potential of the probe was shifted to the more negative zinc potential by the external device. After a further 24 h an electrolyte film of about 1 cm in height had appeared on the nickel strip. An experiment under the same conditions, but in air instead of in diluted hydrogen, produced a film of 1 cm at the cadmium potential and more than 1.5 cm at the zinc potential.

Several authors [5 - 7] have already reported that the electrolyte film consists of two parts. These are an area of drops at the head and an area where the whole of the metal strip is covered by electrolyte. Hull and James [6] called these areas of "fine creep" (area of drops) and "solid creep" (area of complete coverage).

Observation of a growing film under a microscope indicated that the drops appeared to have no origin. At first they are just small spots increasing in size but not changing in position. Adjacent drops can coalesce and finally form a continuous film. During this process new, fine drops appear at the film front. The newest areas of the visible film are at the top, the oldest are just above the bulk electrolyte. This observation suggests that the film is generated by vapour condensation on the metal sheet. The term 'creepage' is unjustified.

Experiments have shown that the film can also be generated in a closed apparatus, where the relative humidity is controlled by the vapour pressure of the bulk electrolyte. If the drops of an electrolyte film consisted of the same concentration of alkali hydroxide, shrinkage rather than growth would occur due to the surface tension.

The mass and concentration of electrolyte in a film has been determined in several experiments. The former by determining the weight of a probe with

and without a film, the amount of alkali hydroxide being titrated. A film generated in 24 h from 6N KOH at the zinc potential on a nickel plate consisted of 9N KOH and had a thickness of 2 μm . These values are representative of a number of experiments. The results varied greatly, yet, in all cases, the alkali concentration in the film was higher than in the bulk electrolyte. The lowest value was 7.2N in the film. The calculated thickness varied between 2 and 7 μm . These variations to a large extent are due to experimental error when determining the weight of the film by calculating the difference of large, incorrect numbers. The films themselves probably show less variation. The results are average values for the whole films.

In a variation of the experiments, the probe was attached to a balance and the apparent weight during film generation was registered. There were indications of a change in wetting force between the electrolyte and the metal, but the phenomenon was not investigated thoroughly.

The fact that the film consisted of electrolyte of a higher concentration than that of the bulk electrolyte suggested a further experiment. Efforts were made to generate a film from a saturated solution (with a sludge of solid hydroxide). Experiments with sodium and potassium hydroxide were inconclusive: the saturation of these solutions is strongly dependent on temperature. An attempt to generate a film from a saturated solution of lithium hydroxide (nickel probe, zinc potential, 24 h) was unsuccessful. A white, solid crust appeared at the probe just above the meniscus. No film was observed above this.

It is known that cells using potassium hydroxide show a greater tendency for leaking than cells with sodium hydroxide. Investigations by Stuart and Davis [7] showed that the speed of growth of electrolyte films from these solutions decreased in the sequence $\text{KOH} > \text{NaOH} > \text{LiOH}$. Mixtures exhibit a continuous transition between the extremes. A correlation between viscosity and film height in a given time has been observed.

In this experiment, the distribution of both ions in a film was investigated, the electrolyte consisting of a mixture with an alkali atom ratio Na/K of 83/17. The overall concentration was 7N in hydroxide. A film was generated on a strip of nickel at the zinc electrode potential within 36 h. It was prepared for investigation by exposure to an atmosphere of carbon dioxide in a desiccator: the hydroxides were converted to carbonates. The solid sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) is a compound which contains a large quantity of water. The film almost instantly turned to slush. Excess water was absorbed by the desiccant.

The ratio of sodium/potassium along the height of the film was investigated by X-ray analysis under a scanning microscope. The results are shown in Fig. 1.

Each point shows the sodium to potassium ratio in a square of 2×2 mm. Three parallel measurements over the height of 12 mm allowed a check for errors. There was a significant increase in potassium content with increasing film height. At the film front, the two alkalis are in almost equal concentration.

The former experiment showed a different migration speed for different cations in a film. In a second experiment, the behaviour of anions was inves-

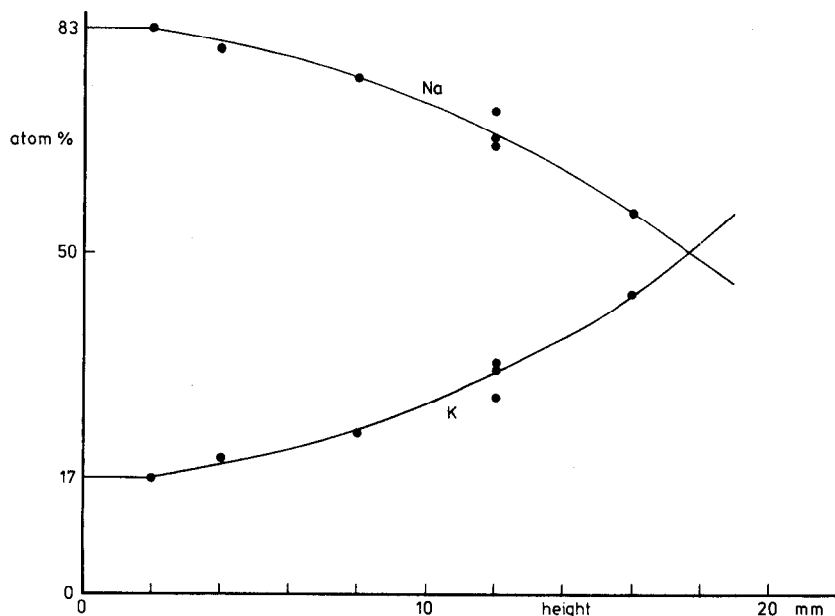


Fig. 1. Distribution of potassium and sodium atoms along an electrolyte-film. The bulk electrolyte contained both ions in the ratio 17:83 ($K^+ : Na^+$).

tigated. A film was generated from a saturated solution of sodium chloride by inserting a nickel plate and connecting it to a large zinc plate in the same electrolyte. Within one day a film showing a strong alkaline reaction appeared on the nickel plate. In a second experiment the film was prepared under CO_2 using the same methods as described above and investigated under a scanning microscope. Figure 2 shows a sequence of photographs taken with this instrument. The film had a height of nearly 12 mm, was generated within 3 days, and apparently consisted of three parts.

The lowest 2 mm showed a crust of cubic crystals of sodium chloride. In this area the electrolyte was wetting the electrode. Above this, there was an area consisting of a thin film of dried electrolyte. This film almost completely covered the metal. X-ray analysis showed a low chloride to sodium ratio of about 96:4 (atom ratio) in this part of the film. Apparently there was a direct connection between this part of the film and the bulk electrolyte. The third part of the film, from 5 mm up to 11 mm, consisted of dried drops, the lower ones large in size and apparently the result of coalescence of smaller drops. With increasing height the uncoated area of the nickel plate increased. At about 10 mm height the film consists of small, apparently unconnected oval-shaped drops. There is no hint of the origin of the electrolyte in this area. No connection between the independent drops could be detected. An exchange of electrolyte *via* small capillaries is not plausible because, in this case, the large drops would grow at the expense of the small drops as a result of surface tension. No chloride could be detected in these drops above 5 mm.

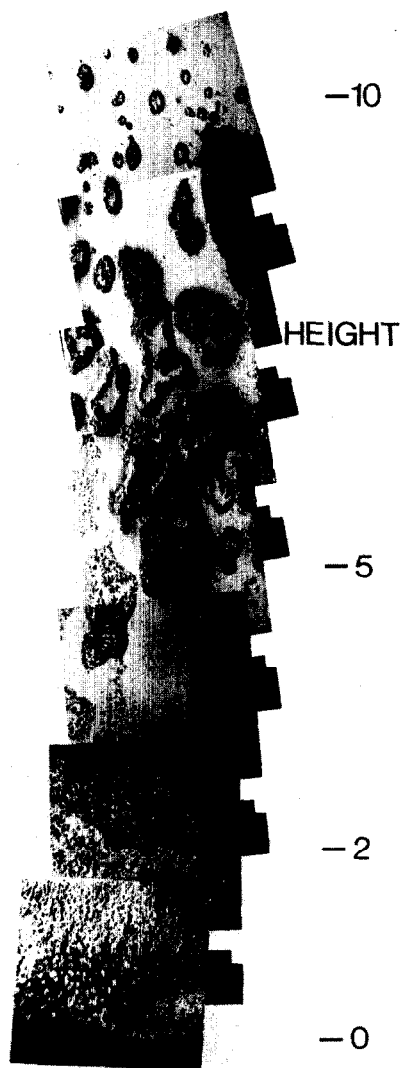


Fig. 2. Sequence of photographs showing an electrolyte film generated on a nickel strip by NaCl solution. The film was prepared by exposure to CO_2 in a desiccator.

Most investigations of electrolyte creep are confined to the important alkali hydroxides. In investigating the phenomenon, the behaviour of organic bases might be of interest. An experiment which used an aqueous solution of tetraethylammonium hydroxide (20%) in water resulted in a film that showed no significant difference in height or optical appearance from films that were generated from a solution of alkali hydroxide.

In a separate experiment, the influence of adsorbed substances on the electrolyte creep was investigated. A nickel plate that had been tempered in

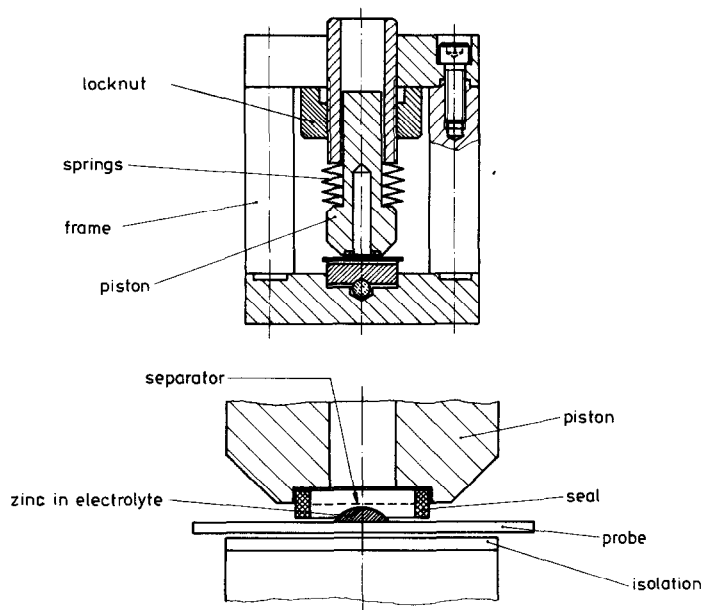


Fig. 3. Apparatus used for the experiments to determine the minimum pressure to prevent electrolyte leakage.

hydrogen was used. The electrolyte was 6N KOH, and the vessel used contained a mixture of 80% air and about 20% carbon monoxide. This gas is rapidly adsorbed by the clean surface of the nickel. After 24 h at the zinc electrode potential, an electrolyte film had formed on the nickel plate that showed no significant differences in appearance or height when compared with a film generated in the absence of carbon monoxide. This experiment was conducted in the hope of finding a significant effect. The conclusion that adsorbed substances have no influence on electrolyte creep is certainly premature.

Electrolyte leakage is, in general, a property of alkaline cells. The new lithium cells with organic electrolyte are considered to be leak proof. In a separate experiment, attempts were made to create a film from an organic electrolyte. The solution consisted of 1M lithium perchlorate in propylene carbonate with 25% dimethoxyethane. The probe consisted of a nickel strip connected to a large plate of lithium in the same electrolyte. With free access of air and humidity a white crust appeared at the phase boundary which was very similar to the crust generated from a saturated solution of lithium hydroxide. No film of any kind was observed above this crust.

The aim of our investigations was the realization of a non-leaking alkaline cell. In addition to the experiments described above, efforts were made to find the minimum seal pressure necessary to stop electrolyte from leaking. The experiments were conducted using the apparatus shown in Fig. 3. A set of springs presses a seal *via* a piston against a probe. The force can be controlled by a locknut. The probe itself is polarised by a small amount of an

electrochemical active material — in general, a few milligrams of zinc or cadmium with electrolyte inside the seal. The piston is isolated from the zinc by a sheet of separating material. The apparatus was assembled in the reverse position. The barrel of the piston contained the electrolyte separated from the active material. Only after application of the required force on the seal and its maintenance with the locknut was the apparatus turned into the upright position. The electrolyte then flowed to the zinc and the experiment commenced.

The seals consisted of small plastic rings of i.d. 9.4 mm and o.d. of 11.5 mm. The sealing surface was 35 mm^2 , the passage for the leaking electrolyte was about 1 mm. All pressures were calculated with these values, although large deformations at high pressure increased the sealing surface. The applied pressure varied from 0.5 N/mm^2 to 150 N/mm^2 , thus by far exceeding the pressure on the seal of a commercial cell.

The assembled apparatuses were stored at 45°C and 90% relative humidity. They were inspected daily by microscope for electrolyte leakage. Unfortunately no exact determination of the amount of electrolyte leakage was possible, but visual comparison made it possible to distinguish between fast, medium, and slow leaks.

The results were astonishing. Although the applied pressure exceeded the values in commercial cells by about one decade, no permanent leakproof apparatus was discovered. Within a few days copper probes showed traces of corrosion outside the seal. These were induced by spots of leaking electrolyte. If the piston contained no electrolyte no corrosion was observed. This effect served as an early warning; it took several weeks or even months before traces of carbonated alkali were visible. Probes of non-corrosive materials, such as nickel and its alloys, could only be judged by traces of carbonate. This fact simulated a longer non-leaking period.

Below a certain minimum pressure the apparatus showed leaking liquid electrolyte within a few hours. The amount was largely dependent upon the pressure — a low pressure resulted in a high leakage rate (Fig. 4.). The limiting pressure for this type of leak was also largely dependent upon the surface quality of the tested material. While for untreated copper the limiting pressure was about 15 N/mm^2 , it was reduced by about 5 N/mm^2 by polishing the surface of the material. Another way to reduce the minimum pressure was to apply a high pressure on the seal while the apparatus was still in the reverse position and maintain this for about 24 h before applying the required pressure and starting the experiment. An even better result was achieved if the seal was glued to the probe. Above the minimum pressure the leakage showed only slight dependence upon pressure.

Two leakage mechanisms are apparent: I, strongly dependent on pressure, surface quality, and showing hysteresis after having been at high pressure for sufficient time for the plastic seal to have adapted to surface contours. This is apparently due to a leak through pores between the seal and the probe. The second mechanism, II, shows only a slight dependence upon pressure, has a comparatively low transportation rate, and is apparently of an electrochemi-

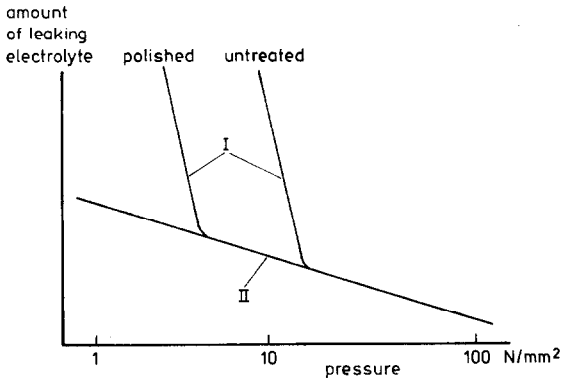


Fig. 4. Amount of leaking electrolyte vs. pressure on the seal. It should be noted that this Figure only gives qualitative results; no absolute values are known and no extrapolation is allowed.

cal nature. Examination of probes showed that mechanism II transports electrolyte under the hole sealing surface. By using a lightly oxidised copper strip it was found that at a pressure of 40 N/mm² the electrolyte had reached half of the sealing zone within 4 h.

An experiment with a semi-transparent mirror of sputtered copper on a piece of glass showed no visible change under the seal, yet the characteristic corrosion on the outside proved that the electrolyte is transported in an extremely thin layer. Only copper and some of its alloys are suitable for experiments at the zinc electrode potential. A number of other materials, mainly nickel and its alloys, but also including titanium, zirconium, and other more exotic materials including vitreous carbon have been investigated. The results showed no significant differences. Experiments with sodium or potassium hydroxide gave practically similar results.

Tests of different sealant materials showed significant differences. The best results were obtained with a polyamide, while polypropylene was among the worst materials. This has not yet been explained because it is a known fact that high humidity increases the leak rate. The material with low water absorbance (PP) should be better than the one with high water contents (PA).

A decrease in pressure due to the relaxation of the plastic seal cannot be held responsible because the set of springs keeps the pressure almost constant.

Conclusion

These experiments have produced new evidence about the nature of electrolyte creep. It is linked to the reduction of either oxygen or water at the electrode. If these reactions are prevented by excluding oxygen and by applying a potential that is more positive than that required for water reduction, no film is generated. If a film is generated, it does not creep up the electrode (although this term is used throughout this article) but it consists of condensed atmospheric moisture on an invisible "prefilm". The latter has a lower water pressure than the bulk electrolyte from which it is generated. All

theories that postulate a film actually creeping upwards from the bulk are incompatible with these results (wetting, Marangoni-effect).

The visible film grows from the top, not the bottom. The higher concentration of electrolyte in the film has been postulated by Baugh *et al.* and Hull *et al.* [6 - 8], but only the latter also postulates growth at the film front by humidity condensation. The origin of the "prefilm" remains unresolved. Hull *et al.* require an adsorbed monolayer of water as an ion-conducting phase on the polarised current collector. Certainly there is some adsorbed water on the electrode (though hardly more than a monolayer), but in this case, the at least partial, replacement of water by carbon monoxide should have a significant effect. Additionally, a monolayer should easily be wetted by the electrolyte yet the film front consists of drops.

Another plausible explanation might be the existence of an ion conducting hydroxide at the surface of the electrode. This might intercalate alkali atoms from the solution, allow them to diffuse upward, and be reoxidised by air or water. This mechanism would produce the very highly concentrated solution of alkali hydroxide required for condensation of water in drops. This model can explain most of the observed properties of the film yet it should be very sensitive to the base material of the current collector. For example, no film should be generated on metals such as gold or platinum because they do not have a surface layer of hydroxide. Any model which does not require a special surface state for the three steps: deposition of alkali — transport by diffusion — reoxidation to hydroxide is plausible. A conceivable theory will be presented in Part II of this paper.

The experimental results suggest the following means of preventing leakage:

- (1) The potential of the negative current collector should be shifted to a more positive value within the sealing zone by some oxidizing material.
- (2) The seal should be in state II (Fig. 4). This state can be attained by using high pressure, very smooth surfaces, or by applying some pore-plugging material such as glue.

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