

ELECTROLYTE CREEPAGE IN GALVANIC CELLS II. TRANSPORT MECHANISM AT HIGH PRESSURES

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Summary

A mechanism for electrolyte creep is presented, explaining the high pressure that the electrolyte film can generate in the sealing zone of an alkaline cell. Also, the drop formation at the film front in creep experiments is explained. We assume that alkali atoms, underpotential deposited from the continuous electrolyte film, diffuse a short distance along the metal surface and again react with air and humidity to form a drop of electrolyte. The velocity of the whole film movement depends on the equivalent conductivity of the alkali ions in the continuous electrolyte film.

Introduction

In Part I of this paper [1] experiments have been described which show that the mechanism driving the electrolyte film between the grommet and the negative cap of an alkaline cell is able to build up high pressures. A number of creep mechanisms have been suggested by several authors [2 - 7], but the origin of these high pressures has not been discovered.

General considerations

A creepage film becomes visible as small drops of liquid, which enlarge and coalesce to form a continuous film. The REM photographs presented in Part I ([1] (Fig. 2)) showed separate drops of electrolyte. Nevertheless, there is transport of material between these surface drops.

The question arises as to why the spots of electrolyte are stable and do not spread all over the metal surface. If a continuous film of electrolyte existed between the drops, they would instantaneously wet the whole surface. Thus, the conclusion must be that the actual film transport takes place within a surface layer the properties of which are determined by the metallic substrate.

From the above considerations it follows that water vapour condensing into the film is unlikely to be the driving mechanism. The drops themselves do not move. Only those mechanisms generating a force along the surface in

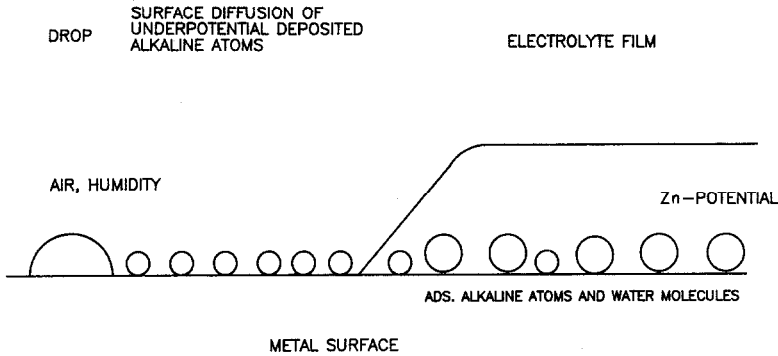


Fig. 1. Schematic view of electrolyte film creepage. At the film front underpotential deposited alkali atoms diffuse along the metal surface, again reacting with air and humidity to form drops of electrolyte.

the direction of the greatest potential gradient are realistic. Baugh *et al.* [6] have suggested the Marangoni effect as an explanation of creepage. However, if there is no free surface, as in the case of a film between the grommet and the cap of a button cell, a surface tension cannot act on the film. Hull *et al.* [5] assume that electro-osmotic movement at least drives the film front. However, the driving mechanism should operate along the whole length of the film, but the electrolyte concentration is too high for electro-osmotic movement.

Two mechanisms are presented in this paper, which we consider to be responsible for creep. A schematic view is given in Fig. 1.

The first model describes the electrochemical creep at the film front by assuming that alkali metal atoms, underpotential deposited from the electrolyte at the potential of Zn or Cd, diffuse along the metal surface and react with oxygen and water vapour to form alkaline electrolyte again.

In the second model migration of ions in the coherent part of the electrolyte film is thought to be coupled to the metal surface, thus generating a high film pressure.

Underpotential deposited alkaline atoms

The deposition of a sub-monolayer of heavy metals from an electrolyte on a foreign substrate, at potentials more positive than the reversible potential for the deposition of the bulk metal, is well known [8 - 13]. This phenomenon is called underpotential deposition.

The underpotential deposition of alkali metals has so far been shown only in the presence of organic electrolytes. Assuming that at similar potentials underpotential deposition also occurs in aqueous electrolytes, then, as

If underpotential deposition and diffusion of alkali metal atoms also hold under our battery conditions, then the following creep mechanism is possible.

At the negative potentials of Cd or Zn, alkali metal atoms are underpotential deposited on the metal surface as a sub-monolayer. The atoms diffuse along the metal surface also passing the electrolyte frontier. Since the alkali atoms were deposited at the Zn or Cd potential, their reactivity is far less than that of the bulk alkali metal. Thus, the alkali atoms do not react immediately with air and humidity, but diffuse a short distance until, *e.g.*, a grain boundary is reached where some water molecules are collected by capillary condensation. There the surface atoms again react with air and the water molecules, and a drop of electrolyte develops on the surface.

Thus, the model explains the formation of drops and, obviously, the generation of high pressures too, which were found experimentally. Using the relation

$$\Delta\mu_{\text{ads}} = pV_{\text{ads}} \quad , \quad (2)$$

where $\Delta\mu_{\text{ads}}$ is the enthalpy of adsorption and V_{ads} the molar volume of the adsorbate, a rough estimate can be made for the film pressure. Assuming $\Delta\mu_{\text{ads}} \approx 3$ eV for the adsorption of alkali atoms on tungsten [15] and a 10% coverage of potassium, *i.e.*, taking roughly the tenfold molar volume of bulk potassium $V_{\text{ads}} \approx 4.50$ cm³/mol, then a pressure of 643 N/mm² is obtained, which is far above the pressures that can be obtained in practice (20 - 30 N/mm² for button cells).

Unfortunately this model, which explains pressure build up and drop formation, is not easily proved. We have found some indication of a non-film structure on examining the "film" by impedance spectroscopy. The results of these investigations will be presented in a later publication.

Since the potential gradient within the zone of fine creep is high this zone has only a small extension. The creep velocity is determined by the continuous film which develops from enlarging and coalescing drops.

Transport in the continuous film

It is generally accepted that electrochemical creep is caused by a potential gradient in the film. A current, J , flows and, according to their transport numbers, cations and anions move within the film. The alkali ions are hydrated and carry a large volume of H₂O, in contrast to the OH⁻ ions which mainly move by proton jumps from water molecules to OH⁻ ions.

In aqueous electrolytes the reduced metal surface is usually covered by a fixed layer of water molecules. Since the transport of OH⁻ ions takes place by proton jumps from water molecules to OH⁻ ions, their movement near the metal surface is coupled to this surface, causing a relative movement of OH⁻ ions, according to their transport number, with respect to the metal surface.

The current flowing in the film causes an electric field acting on the ions. In a free electrolyte the forces on the positive and negative ions are in equi-

librium and no extra movement of electrolyte takes place. However, near the metal surface the movement of the negative ions is assumed to be coupled to the metal, so that now the cations moving relative to the metal surface can produce a pressure, p , which is calculated to be

$$p = cF\Delta\psi \quad (3)$$

Here c represents the concentration of the cations, F the Faraday number and $\Delta\psi$ the potential difference along the film.

Roughly assuming $\Delta\psi = 1$ V as the potential difference along the film and the concentration of the electrolyte as 6 mol/dm^3 , the pressure is similar to that calculated for the underpotential deposited film, about 600 N/mm^2 . The sealing pressure must be greater than 600 N/mm^2 to stop film creepage. Because of the limited mechanical strength of the metallic parts of the button cells a sealing pressure of only about $20 - 30 \text{ N/mm}^2$ is possible. Therefore it is not possible to stop film creep propagation by mechanical means alone.

Under these conditions the velocity of positive ions in the film is

$$v_K = \frac{n_K}{c_K} \frac{i}{F} \quad (4)$$

where n_K is the transport number of the cations and i the current density. Assuming a constant voltage drop $\Delta\psi$ along the film, one can write

$$v_K = \frac{n_K \kappa}{c_K F} \frac{\Delta\psi}{l} \quad (5)$$

where κ is the specific conductivity of the electrolyte and l is the length of the film.

Introducing the equivalent conductivity Λ_i of the cations

$$\Lambda_i = \frac{n_K \kappa}{c_K} \quad (6)$$

one gets

$$v_K = \Lambda_i \frac{\Delta\psi}{Fl} \quad (7)$$

Since the film cannot move faster than the cations in the film, v_K determines the velocity with which the creep film moves forward. From eqn. (7) one concludes that the creep velocity should depend on the equivalent conductivity of the cations.

Hull and James [5] have shown that the creep height increases as the equivalent conductivity of the cations increase. The observed dependency on the viscosity of the alkaline electrolyte results from the viscosity dependency of the equivalent conductivity.

It should be mentioned that in our derivation we assumed that the increase in electrolyte concentration at the film front is always compensated for by condensation of humidity from the bulk electrolyte.

Conclusion

Two mechanisms have been presented: The first is based on the hypothesis of underpotential deposition of alkali atoms on the metal surface and describes the behaviour at the film front. It explains drop formation and build up of high pressures. The second mechanism is dominant in the continuous film and explains the dependency of film velocity on the equivalent conductivity of the cations.

Naturally, the models simplify the complexity of the real situation, but we think that they are in good agreement with present knowledge on film creep.

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